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16. ABSTRACT

A completely mixed anaerobic filter was found to effectively remove organic matter concentrations in high-strength solid waste leachate over a range of organic loadings and shockloads. Recirculation eliminated the need for buffer solutions. Testing of a fixed film biological reactor model showed that the substrate removal rate is primarily affected by substrate concentration, specific surface area, flow rate, and temperature of the unit. Studies of the biological aerated lagoon or extended aeration process were conducted in six completely mixed reactors (no recycle) fed with undiluted leachate. Phosphate requirements of the aerobic biomass were extensively evaluated. Kinetic constants were calculated for optimum conditions. The settling and dewatering characteristics of the sludge from the aerated lagoons were studied. The combined treatment of leachate and municipal sewage in a conventional plugflow activated sludge unit was found to effectively treat high strength leachate. The test unit was not able to treat the high strength leachate at $\geq$ 4% of the municipal sewage flow rate. Physical-chemical treatment methods are not effective in removing large quantities of organics from the leachate and that biological pretreatment is required; these methods were therefore tested using aerated lagoon effluents. Ozonation, activated carbon, anion exchange resins, and reverse osmosis were studied. Treatment costs were estimated for leachate flows of 7.6 and 76 ℓ/min containing 5000 and 25,000 mg/ℓ BOD_5.

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Volume II

Biological and Physical-Chemical Processes

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

This study involved extensive analysis of different organics and inorganics present in leachate samples from landfills located in different regions of the United States. These analysis were then used to predict the effectiveness of different biological and physical chemical treatment methods for contaminant removal.

Francis T. Mayo, Director
Municipal Environmental
Research Laboratory

ABSTRACT

The efficiencies of three different types of biological treatment units in removing organic matter from solid waste leachate were extensively evaluated. The units studied were the anaerobic filter, the aerated lagoon, and an activated sludge unit treating combined leachate and municipal sewage. The effectiveness of physical-chemical treatment steps in further removing organic matter from the biological unit effluents was also examined.

A completely mixed anaerobic filter, in which the influent is diluted with recirculated effluent, was studied for a 52-day period and found to effectively remove organic matter concentrations in high-strength, solid waste leachate over a range of organic loadings and shockloads. Recirculation increases the acidic pH of the feed, eliminating the need to add the costly buffer solutions required in plugflow anaerobic filters. Ninety-nine percent of the COD removed in the unit was accounted for in the methane produced. This valuable energy source can be used for combustion to heat the unit. A microbial solids balance indicated that only 0.012 grams of VSS was produced per gram of COD removed. Because of the low solids production and initial seeding of the unit with digested sludges, it was not necessary to add nutrients. Although a possible heavy metal toxicity was observed, it was eliminated by adding sulfide. A high organic matter removal percentage was observed at hydraulic detention times greater than 7 days, but the percentage was considerably lower at shorter detention times. Increases in organic loading had a substantial effect on the relative organic matter composition of the effluent. Testing of a fixed film biological reactor model showed that the substrate removal rate is primarily affected by substrate concentration, specific surface area, flow rate, and temperature of the unit.

Evaluation of various physical-chemical treatment methods such as chemical precipitation, activated carbon adsorption, and chemical oxidation showed that these methods were not very effective in removing organic matter from high strength leachate. Although free volatile

fatty acids, present in large quantities in leachate, have a relatively low activated carbon adsorption capacity, even lower capacities were noted for the non-fatty acid fraction using batch isotherms. Although relatively high organic matter removals were obtained using activated carbon columns, rapid breakthrough occurred after passage of the initial bed volume of effluent. Activated carbon treatment of the high strengh leachate was found to be unfeasible because of rapid headloss buildup resulting from the formation of iron precipitates in the carbon column. These solids are difficult to remove in subsequent backwash operations. The organic matter removal rate achieved using lime precipitation was as low as 26% and was realized only at very high dosages.

Substantially higher adsorptive capacities were observed for biologically pretreated leachate. Removal of biodegradable organics with an anaerobic filter increased the adsorption capacity by 50%, while aerated lagoon treatment of the anaerobic filter effluent resulted in an adsorptive capacity 2.5 times higher than that of untreated leachate. Membrane fractionation of the anaerobic filter effluent followed by activated carbon column treatment of each fraction produced relatively low removal rates for both the high-molecular-weight organics collected in the 18,000 MW UF retentate and the low-molecular-weight organics present in the 150 MW RO permeate. The highest removals were observed for the intermediate-molecular-weight fulvic-like organics which were also characterized by a high aromatic hydroxyl group content. Aerated lagoon treatment of the anaerobic filter effluent resulted in organic matter removals as high as 79% using activated carbon columns. This increased removal rate was shown to result from the higher adsorption characteristics of the low molecular weight organics present in the 150 MW RO permeate. Anaerobic filter treatment of the leachate resulted in lower organic matter removal rates than were obtained with untreated leachate. Aerated lagoon treatment of the anaerobic filter effluent resulted in a slightly higher TOC removal of efficiency. Both removal rates, however, were obtained only at very high lime dosages, precluding the use of this treatment method as a feasible alternative to activated carbon. It was therefore concluded that physical-chemical treatment methods are only effective after extensive biological pretreatment. Of all physical-chemical methods tested, activated carbon treatment was the most effective in removing organic matter.

Studies of the biological aerated lagoon or extended aeration process were conducted in six completely mixed reactors with no recycle fed with undiluted leachate and maintained at detention times of 85.7, 60, 30, 15, and 7 days. These units were operated for periods from 70 to 150 days. The resulting average TOC removal efficiencies varied between 99% and 96.8% at organic loadings ranging from 0.224 $kg/m^3 \cdot day$ (14 lb TOC/1000 cu ft·day) to 1.65 $kg/m^3 \cdot day$ (105 lbs TOC/1000 cu ft·day). The phosphate requirements of the aerobic biomass were extensively evaluated. The 30 day aerated lagoon did not show any deterioration when the COD:P ratio in the influent was increased from 165:1 to 300:1. A significant increase in effluent TOC values was observed, however, when the ratio was increased to 800:1. Such low ratios did not affect the 60 day and the 87.5 day units, which were able to function at a ratio as high as 1540:1; the sludge settling characteristics, however, deteriorated substantially at this ratio. Cessation of nutrient addition to the units having relatively low detention times caused an immediate increase in effluent organic matter concentrations and a decrease in MLVSS. Calculations using the effluent data and MLVSS values obtained under optimum conditions indicated that the bacteria yield was 0.42 mg VSS/ mg COD, the respiration rate content was 0.025 day^{-1}, and the overall first-order substrate removal rate constant was $4.9 \cdot 10^{-4}$ liter/mg VSS·day. All units showed high heavy metal removal rates, especially for iron (99.9%), while low rates were observed for calcium (99.3%) and magnesium (75.9%). The lowest removal rates were obtained with sodium (24.1%) and potassium (17.0%).

The settling characteristics of the sludge from the aerated lagoons were found to be comparable to those of lime softening sludge and primary sludge, which have higher settling rates than observed for secondary sludge. The interface settling rates generally decreased during conditions of nutrient limitations. The dewatering characteristics of the sludge were greatly improved by adding cationic polymers and inorganic coagulants. An increase of approximately 20 times in specific resistance was obtained at a polymer dosage of 1.5% (Nalco 73C32) and 2.3% (Primafloc C_7) and at coagulant dosages of 14.8% ($FeCl_3 \cdot 6H_2O$) and 23.7% ($Ca[OH]_2$). These increases generally corresponded to increases of 6 times in vacuum filler yields. Analysis of the effluent of the 30 day aerated lagoon showed that 97.6% of the organics had molecular weights greater than 100, with 33% in the range from 100 to 500, 41% in the range from 500 to 5000, 20% in the range from 5000 to 50,000 and 4% greater than 50,000, indicating that these organics are amenable to reverse osmosis and activated carbon treatment but not to chemical precipitation.

It was also found that physical-chemical treatment methods are not effective in removing large quantities of organics from the leachate and that biological pretreatment is required. Several physical-chemical methods were therefore tested using the aerated lagoon effluents. While ozonation removed only 48% of the lagoon effluent TOC after a 3 hour treatment period, activated carbon columns were able to remove 86% of the organic matter using an empty bed detention time of 3.7 minutes. A maximum initial COD removal of 53% was realized with a weak base anion exchange resin, while 82% and 85% of the COD was removed using strong base anion exchange resins. Membrane reverse osmosis was the only process capable of removing 91 to 96% of the salts initially present at a TDS concentration of 6200 mg/l. The organic matter removal rates using reverse osmosis ranged from 86% to 97%. These rates were not enhanced by ion exchange or activated carbon pretreatment. Removal of suspended solids by sand filtration or chemical precipitation is likely required for reverse osmosis, activated carbon, or anion exchange resin treatment of the aerated lagoon effluent.

The combined treatment of leachate and municipal sludge was evaluated in a conventional plugflow activated sludge unit. It was found that the test unit could effectively treat the high strength leachate. Directly after the addition of leachate the effluent BOD and COD concentration deteriorated somewhat, but after sufficient adaptations the effluent qualities were generally comparable to that of the control units. While BOD values were not greatly affected, COD concentrations showed a gradual

increase as more leachate was added. The test unit was not able to treat the high strength leachate at 4% of the municipal sewage flow rate, as evidenced by high effluent BOD values and deteriorating sludge conditions. This failure was attributed to limiting phosphate concentrations in the influent and the relative composition of the soluble high molecular weight organics which tend to affect the flocculation of the sludge.

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RECOMMENDATIONS FOR FURTHER RESEARCH

Biological methods of high-strength leachate treatment which were not evaluated because of budget constraints included the fixed media unit (trickling filter and rotating disk), the anaerobic lagoon, and modified soil treatment system currently being tested at the University of Illinois. It is therefore recommended that these systems be studied on a laboratory scale before being applied at the demonstration level.

Much research is needed to optimize the design and operation of anaerobic filters. The type of solid media to which the bacteria are attached should first be studied in a series of parallel tests using various soft materials and shapes. The substrate removal efficiency over a range of loadings should be evaluated and the amount of solids leaving the unit through the effluent should be determined. The second phase should evaluate different feed configurations, such as conventional plugflow feeding, step feeding, and tapered step feeding and the location of the recirculation outflow. Different filter shapes (heights and widths), all having the same volume, should be tested for a given volume, since a low but long unit is less expensive than a low but wide unit, and the amount of substrate removed is likely to be higher in the latter unit. The third phase of the study should focus on operational modes of the filter, and the effect of different recirculation flowrates and operating temperatures should be tested in parallel.

An extensive study should be conducted to determine when leachates are sufficiently biologically stabilized to be effectively treated by physical-chemical methods. The study should combine an in-depth organic chemical analysis of different leachate samples with a limited treatability study.

Finally, research should be undertaken to evaluate combined physical-chemical and biological methods, such as biological aerated lagoons to which powdered carbon is added or activated carbon upflow columns in which a biomass is maintained. The application of such treatment methods could enhance the life and flexibility of leachate treatment units already constructed and in operation.

I

TREATMENT OF A HIGH STRENGTH SOLID WASTE LEACHATE WITH A COMPLETELY MIXED ANAEROBIC FILTER

CONCLUSIONS

A completely mixed anaerobic filter, in which the influence organic matter concentration is diluted with recirculated effluent, was found to effectively remove organic matter concentrations in high strength municipal solid waste leachate at a range of organic loadings and shockloads. Recirculation can effectively increase the acidic pH of the feed to a pH value close to the optimum, thus eliminating the addition of costly buffer solutions as is required for the plugflow anaerobic filter. In the anaerobic filter, complex organics in the feed are hydrolyzed, first by acid fermenting bacteria to free volatile fatty acids, primarily acetic-and butyric acid, which in turn are removed by methane fermenting bacteria and converted to methane (CH_4) and carbon dioxide (CO_2). The methane in the generated gas accounted for 93 percent of the COD removal in the unit, while a solids balance indicated that only 0.012 g VSS was produced per g COD removed. Due to the low solids production and the initial seeding of the unit was digested sludge no nutrient additions were required during the 518 day period even though the COD:P and COD:N ratios in the feed were as high as 4360:1 and 39:1, respectively. Although a possible heavy metal toxicity, likely the result of high copper concentrations, was observed in the unit, this was eliminated after sulfide addition.

A high percentage of organic matter removal was observed when the hydraulic detention time was maintained above 7 days, but, showed considerably lower removal percentages below this detention time. Increases in organic loading had a substantial effect on the relative organic matter composition of the effluent and the magnitude of the fatty acid fraction showed a pattern inverse to that of the nitrogenous organics. A fixed film model was formulated which indicated that at high substrate concentration the substrate removal rate is proportional to the square root of the substrate concentration and the specific area of the filter medium. A comparison of the biofilm model and the measured effluent concentrations tended to indicate that the substrate removal rate is primarily affected by substrate concentration, specific surface area, flow rate and temperature of the unit.

INTRODUCTION

It has been recognized that biological removal of organics in high strength wastewaters is most economically realized in anaerobic biological systems, since these systems do not have the high energy needs associated with aeration as required in aerobic biological systems (Metcalf and Eddy, 1972). As the cell yield in anaerobic systems is about ten to twenty times lower than that in aerobic systems, the costs of sludge disposal are greatly reduced. During anaerobic fermentation the acid-fermenting bacteria degrade the complex waste to free volatile fatty acids, primarily acetic and propionic acid, which are subsequently converted by the methane fermenting bacteria into methane and carbon dioxide. The generated gas can be combusted to yield valuable energy.

A major disadvantage of the anaerobic fermentation is the sensitivity of the anaerobic bacteria which are inhibited at acidic pH values. In addition, the acid- and methane-fermenting bacteria can experience heavy metal toxicities. Such inhibitions will reduce the biological growth rate and result in their subsequent wash-out. An ideal process is therefore one which is able to retain biological solids independent of the waste flow and maintain sufficient high solids concentration for long periods of time. Such an objective is realized by employing a solid media in the unit to which bacteria can attach. Coulter *et al.* (1954) for example, employed an anaerobic filter filled with rock media to retain solids from an anaerobic digester effluent. Although the majority of the BOD was removed in the preceeding digester, additional removal was observed in the filter. Young and McCarty (1967, 1968, 1969) developed the upflow anaerobic filter in which the anaerobic bacteria are present in a film attached to a rock medium to remove organics in the waste flowing upward through the column. Attachment to the medium results in sludge ages of more than 600 days (Young and McCarty, 1968, 1969) and 150 days (Plummer *et al.*, 1968). The unit can therefore be operated at temperatures substantially below 35°C which decreases the bacterial growth rate while still maintaining a sufficient biomass. Upflow anaerobic filters have been built in England since 1876 to purify sewage but the organic removal was mainly thought to be due to adsorption (Truesdale *et al.*, 1961). The removal of organics in septic tank effluent by bacteria attached to soil particles is based on a similar principle.

The removal efficiencies of the anaerobic filter can be higher than those obtained with anaerobic digesters operated at the same volumetric loading. A comparison of the filter with a digester both maintained at a loading of 1.28 kg COD/m^3 day (80 lb COD/1000 cu ft day) showed that the effluent COD of the anaerobic filter was only one fifth of that of the digester effluent (Foree and Reid, 1973). Tadman (1973) noted that an aerobic filter produced an effluent concentration one tenth of that of an anaerobic digester maintained at the same hydraulic retention time of 2 days. Although Chian and DeWalle (1976) showed that the COD removal in the filter was slightly less than observed in aerated lagoons treating the same waste, the color removal and suspended solids removals, however, are comparable. Moreover, the installation and operating costs of the anaerobic filter are about half of that of an aerated lagoon (Pailthorp *et al.*, 1971).

In a plug flow reactor, the pH decreases initially as a result of the acid fermentation, and then increases in the direction of the flow, due to the biological removal of the generated fatty acids, formation of ammonia and reduction of sulfates. Since the acidic pH in the bottom section of the filter can potentially inhibit the methane fermenting bacteria, substantial amounts of buffer solutions are added to the influent waste stream to prevent such pH decrease. El-Shafie and Bloodgood (1973), for example, added 8,000 mg/ℓ $NaHCO_3$ to the influent having a COD of 11,800 mg/ℓ in order to maintain a pH above 6.5. Young and McCarty (1968, 1969) added $NaHCO_3$ at a concentration of about half of the COD content of the waste, whle Taylor (1972) added 1,000 mg/ℓ $NaHCO_3$ at an influent concentration of 8,800 mg/ℓ COD.

A completely mixed anaerobic filter would not experience the pH decrease observed in plug flow units, since the mixing maintains a fairly uniform pH throughout the depth of the filter. This in turn would eliminate the need for adding costly buffer solutions. In a completely mixed filter, a major part of the effluent is returned and mixed with the influent stream. If the effluent has a sufficient bicarbonate buffer capacity, it is even able to neutralize feed solutions with an acidic pH. Since all of the previous studies with anaerobic filters used once through plug-flow reactors, the present study was conducted to evaluate a completely mixed anaerobic filter.

The high strength acidic wastewater evaluated in this study was a solid waste leachate containing free volatile fatty acids and complex high-molecular-weight carbohydrate-like organics (DeWalle and Chian, 1974) to give a COD of 54,000 mg/ℓ and a pH of 5.4. The fatty acids represented 49 percent of the total COD, while 1610 mg/ℓ carbohydrate, 605 mg/ℓ tannins and 1270 mg/ℓ proteins were also detected. Such leachate is generated in solid waste landfills when infiltrating rainwater allows degradation of primarily cellulosic materials. Collection and treatment of such leachate alleviates the potential problem for groundwater pollution. Due to leaching of metal objects, relatively large amounts of potentially toxic heavy metals were also detected in the leachate used in the present study. The observed concentrations were 2,200 mg/ℓ Fe, 104 mg/ℓ Zn, 18 mg/ℓ Cr, 13 mg/ℓ Ni and 0.5 mg/ℓ Cu.

OBSERVED SUBSTRATE REMOVAL IN FIXED FILM REACTORS

An engineered design of the anaerobic filter requires a knowledge of the substrate removal kinetics in fixed film biological reactors. Such information is obtained when the influent substrate concentration and the hydraulic detention time are varied independantly of each other while the system response is studied. Schulze (1960) noted that the percentage of BOD removal did not change with the increasing influent concentration when an aerobic fixed film reactor was maintained at a constant hydraulic loading. However, when the hydraulic loading was increased and the influent concentration maintained, the percentage removal decreased, indicating that the percentage removal was solely determined by the detention time in the filter. The detention time is a function of hydaulic loading and depth of the filter. The observed results thus follow the first order substrate removal kinetics.

Rinke and Wolters (1970) also varied influent concentration and hydraulic loading independently of each other in aerobic trickling filters and noted that, at a constant hydraulic loading, an increase in influent substrate concentration corresponded to a constant percentage of removal at low organic loadings but showed a decreasing percentage of removal at high loadings. Maintaining a constant organic loading by increasing the hydraulic loading and simultaneously decreasing the influent concentration resulted in a constant amount of substrate removed and a constant percentage substrate removal. Cook and Kincannon (1970) showed, in contrast to Schulze (1960), that at a constant hydraulic loading an increase in influent concentration resulted in a lower percentage substrate removal. Similar to Rinke and Wolters (1970) they noted that at constant organic loading the percentage of removal did not change when the hydraulic loading was increased and the influent concentration was decreased simultaneously. Based on these data one would conclude that recirculation of the effluent to reduce the influent concentration would be beneficial since this would result in a same percentage COD removal with respect to the diluted influent. When the substrate concentration of the effluent is small as compared to the influent concentration, recirculation would then result in a lower actual effluent concentration.

Less variable results have been obtained in evaluating anaerobic filters. Young and McCarty (1968, 1969) showed that increasing the influent concentration at constant but low hydraulic loading resulted in a constant percentage removal but showed a decreasing percentage at high hydraulic loadings. Maintaining the organic loading while decreasing both the influent concentration and the hydraulic detention time resulted in a constant percentage removal at low organic loadings and a decreasing percentage at high organic loadings. The actual effluent concentration, however, was only determined by the organic loading and was independent of influent concentration. Caudill (1968) similarly noted that the COD removal efficiency in an anaerobic filter treating potato starch waste remained at 77 percent when the influent concentration increased from 500 to 1000 mg/COD at constant hydraulic loading. El-Shafie and Bloodgood (1973) also observed a constant percentage removal independent of the influent concentration at a given hydraulic loading. Jennett and Dennis (1975) found that at a constant organic loading of 3.5 kg COD/m^3 day (220 lb COD/1000 cu ft day) the percentage removal decreased from 98 percent to 95 percent and 94 percent respectively when the influent concentration decreased from 16,000 mg/ℓ to 8,000 mg/ℓ and 4,000 mg/ℓ. The observation that the actual effluent concentration also decreased, would indicate that recirculation could result in slightly lower effluent concentrations.

The above considerations are important in evaluating the effect of recirculation on substrate removal efficiency as practices in the present study. Based on fundamental considerations, both Schulze (1960) and Germain (1964) concluded that recirculation would have no effect on organic matter removal. However, both Eckenfelder (1961) and Gallar and Gotaas (1964), using a large number of actual aerobic trickling filter plant data, concluded that recirculation resulted in a larger percentage substrate removal possibly due to the inoculation of the incoming sewage with bacteria present in the effluent. Several studies compared treatment efficiency before and after recirculation was practiced and generally noted an improvement in effluent quality. Moore *et al.* (1950) noted that a recirculation ratio of one improved the BOD removal from 85 percent to 93 percent at an influent BOD of 240 mg/ℓ. Using a similar recirculation ratio Hanumanula (1969) noted that the BOD removal increased from 62 percent to 91 percent at an influent BOD of 330 mg/ℓ. Oleszkiewics (1974) showed that recirculation is especially beneficial at high influent substrate concentrations due to better aeration of the liquid film and the elimination of substrate inhibition. He observed an improvement of the removal from 30 percent to 85 percent at a recirculation ratio of 5 using an influent COD of 3,000 mg/ℓ.

SIMULATION OF SUBSTRATE REMOVAL IN BIOFILMS

The substrate removal kinetics in fixed film biological systems can either be described in terms of substrate concentrations existing in the bulk liquid phase or simulated substrate concentrations in each layer of the biofilms, the sum of which predicts the response of the entire film. Kornegay and Andrews (1969) and Young and McCarty (1968, 1969) used the former approach; the latter authors introduced a substrate gradient factor defined as the ratio of the concentration at the liquid-biofilm interface to the effective concentration in the biofilm. As a result, the calculated apparent half velocity concentrations are several times larger than would be obtained if all bacteria were complete dispersed. Recent studies however, generally use the second approach in which the process of substrate diffusion and bacterial uptake are simulated for each of the successive layers of the biofilm; the present study used a similar approach.

In a biological film reactor at steady state, a mass balance within the film can be made by equating:

$$\text{input - output = uptake} \qquad (1)$$

According to Fick's law of molecular diffusion the mass transfer rate dF/dt through a surface area A is proportional to the concentration gradient of the substrate S at the interface:

$$\frac{\partial F}{\partial t} = - A\, D_s \frac{\partial S}{\partial z} \qquad (2)$$

$\frac{\partial F}{\partial t}$ = rate of mass transfer at interface (mass/time)

D = diffusion coefficient (length^2/time)

$\frac{\partial S}{\partial z}$ = substrate concentration gradient (mass/length^4)

z = depth of biofilm starting from liquid-film interface (length)

A = surface area of biofilm (length^2)

The biological uptake within the biological layer can be expressed as:

$$\frac{dS_z}{dt} = \frac{US_zX}{K_s + S_z} \tag{3}$$

$\frac{dS_z}{dt}$ = rate of substrate uptake (mass/length^3 time)

U = maximum substrate removal rate $\left(\frac{\text{mass of substrate}}{\text{mass of biomass} \cdot \text{time}}\right)$

S_z = substrate concentration at depth z (mass/length^3)

X = biomass concentration within the biolayer (mass/length^3)

K_s = half velocity concentration (mass/length^3)

By making a material balance between a differential distance within the biolayer using equations (1), (2) and (3), it results in the following equation for a unit cross sectional area:

$$\frac{d^2S_z}{dz^2} = \frac{1}{D_x} \cdot \frac{US_zX}{K_s + S_z} \tag{4}$$

which states that the second derivative of the substrate concentration with respect to z is dependent on both the substrate and biomass concentration. When axial dispersion becomes important the term $v \cdot \frac{\partial S}{\partial z}$ will have to be added to the right hand side of Equation (4). However, since the filter media in the present study consists of long curved channels, this term can be omitted.

Equation (4) is a second order non-linear differential equation. As such it does not have a simple solution. However the equation can be solved when S_z is either much larger or much smaller than K_s (Hang and McCarty, 1971). When S_z is much larger than K_s Equation (4) reduces to a zero order kinetic equation;

$$\frac{d^2S_z}{dz^2} = \frac{UX}{D_s} \tag{5}$$

which can be integrated for a unit cross sectional area, and the mass transfer rate at the interface becomes:

$$\frac{dF}{dt} = UXh \qquad (6)$$

h = thickness of biofilm (length)

Since for a given waste, U and X are not expected to vary greatly, equation (6) would indicate that the rate is independent of substrate concentration but directly proportional to surface area and thickness of the biolayer. In such a situation the decrease of substrate within the biofilm is small as compared to the concentration at the interface so that the rate of substrate utilization per unit of biomass is approximately the same as if the solids were evenly dispersed throughout the liquid. According to Pirt (1973) and Saunders and Bazin (1973) the thickness of the biolayer can be approximated by

$$h = \frac{2D_s \cdot S_b}{UX} \qquad (7)$$

S_b = substrate concentration in bulk liquid (mass/length^3)

However, equation (7) was derived based on the boundary conditions of zero substrate concentration at the interface of the biolayer and the solid support; it therefore violates the constraint that S_z is much larger than K_s and is therefore only an approximation. Since D_s, U, and X are not expected to vary to a great extent for a given substrate, Equation (6) can therefore be further modified to indicate that the rate of substrate removal per unit reactor volume is related to the specific surface area, A/V, and the square root of the bulk substrate concentration:

$$\frac{dF}{Vdt} = k_1 \cdot \frac{A}{V} \cdot \quad S_b \qquad (8)$$

k_1 = coefficient based on zero order kinetics (mass$^{\frac{1}{2}}$/length$^{\frac{1}{2}}$·time)

V = reactor volume (length^3)

An equation similar to equation (8) was also used by DeWalle and Chian (1976) to describe the rate of biological regeneration of activated carbon particles due to the presence of activated sludge solids. It is realized that at very high substrate concentrations the rate of substrate removal will be independent of the substrate concentrations due to the zero order kinetics of the reaction. In that case the rate of substrate removal will only be dependent on the specific surface area in the reactor.

When S_z is much smaller than K_s, equations (4) reduces to a first order kinetic equation:

$$\frac{d^2S_z}{dz^2} = \frac{UXS_z}{D_s \cdot K_s} \tag{9}$$

Which after integration yields the mass transfer rate equation at the interface:

$$\frac{dF}{dt} = S_b \quad \frac{D_s\ UX}{K_s} \tag{10}$$

Since D_s, U, X and K_s are not expected to vary greatly with a given substrate, Equation (10) reduces to

$$\frac{dF}{Vdt} = k_2 \cdot \frac{A}{V} \cdot S_b \tag{11}$$

k_2 = coefficient based on first order kinetics (length/time)

The equation indicates that the rate of substrate removal per unit reactor volume is related to the specific surface area of the biofilm and the bulk substrate concentration, but is independent of film thickness. A similar equation has been given by Atkinson and Daoud (1968) for large film thickness. Equations (8) and (11) should be used in small successive sections in plug flow anaerobic filter columns. However, since such detailed data are generally not available, both equations can be used with respect to the whole column while S_b is substituted by the effluent concentration of the column.

Additional resistance to mass transfer from the bulk liquid to the liquid-biofilm interface is caused by the liquid film adjacent to the biofilm. The thickness of this layer can be described by the Nusselt (1916) equation:

$$\delta = [\frac{3\ \nu\ Q}{\rho\ g\ W}]^{1/3} \tag{12}$$

Q = flow rate (length^3/time)
ν = viscosity (mass/time·length)
ρ = density of liquid (mass/length^3)
g = gravitational constant (length/time^2)
W = width of film (length)
δ = thickness of film (length)

Since the mass transfer rate decreases with increasing liquid film thickness in the laminar sublayer, the flux of substrate would also be proportional to the flow rate to the power 1/3. This agrees with the analysis by Takeshi *et al.* (1972) that the mass transfer coefficient K_L for laminar flow can be expressed as:

$$K_L = kQ^{1/3} \text{ for Re} < 10 \text{ and} \tag{13}$$

$$k_L = kQ^{1/2} \text{ for Re} > 10 \tag{14}$$

Both equations (8) and (11) illustrate the importance of the specific surface area, A/V, of the fixed film reactor. Based on similar considerations Ames *et al.* (1962) stated that the substrate removal was proportional to the specific surface area of the media. Lamb and Owen (1970 came to the identical conclusion. For the above reasons, a filter medium with a relatively high specific surface area of 206 m^2/m^3 (63 ft^2/ft^3) was selected for the present study.

MATERIALS AND METHODS

The laboratory scale anaerobic filter column was constructed of Plexiglas with an overall height of 246 cm and 20.2 cm OD (Figure 1). The height of the filter medium in the column was 199 cm and comprises a volume of 54.6 liter (1.93 cu ft). A head space of 1.4 liter is provided at the top of the medium while the inlet section is 2.8 liter. A solids collection device, installed at the end of the second period in Phase II, is located at the bottom of the column and has a volume of 3.8 liter. A recirculation surge vessel with a volume of 5.2 liter provides the separation of the effluent stream and the recirculation stream. The latter is subsequently used to dilute the incoming leachate and raise its pH. The total volume of the column is therefore 67.8 liter of which 54.6 liter or 81 percent contains the filter medium to which the bacteria are attached.

The medium in the column consists of plastic "Surpac" slabs (Dow Chemical Midland, MI) while additional plastic strips were placed between each sheet. The plastic material has a specific density of 1.45 g/cm^3. As the average thickness of the slab is 0.57 mm, on the basis of 100 measurements, the specific surface of the plastic material itself is therefore 3490 m^2/m^3 (1067 ft^2/ft^3). The specific surface area of the media per unit column volume is 206 m^2/m^3 column volume (63 ft^2/ft^3 column volume); the total surface area in the column is therefore 11.3 m^2 (121.6 ft^2) and only 6 percent of the column volume is taken up by the plastic material resulting in a porosity of 94 percent. A comparable study by Young and McCarty (1968, 1969) used smooth quartzite stones with a porosity of only 42 percent and a specific surface area of 114 m^2/m^3 column volume (37.5 ft^2/m^3 column volume) as estimated from data provided by Truesdale *et al.* (1961).

The leachate employed in this study was obtained from a lysimeter filled with solid waste to which simulated rainwater was added (Chian and DeWalle 1976). After collection from the lysimeter, the leachate was refrigerated

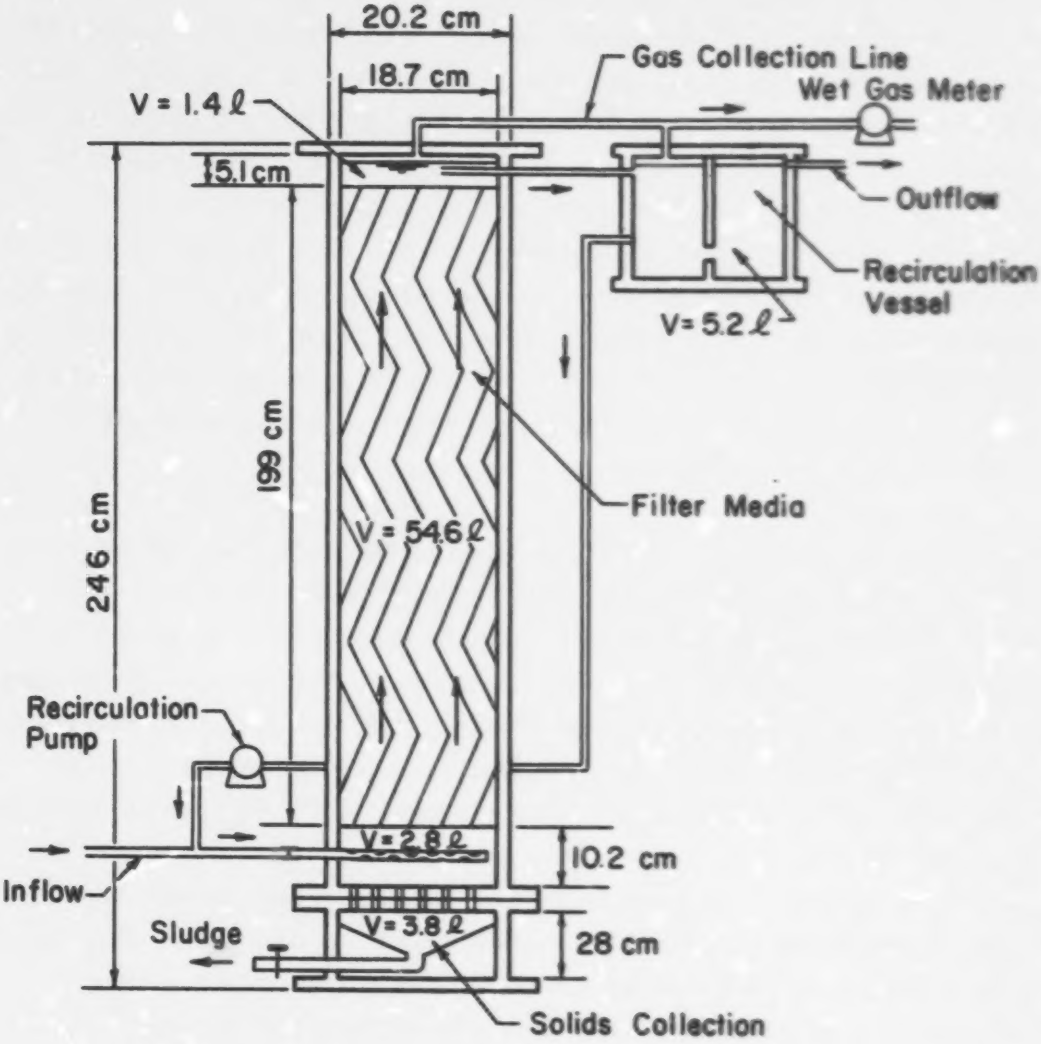
20.2 cm
18.7 cm
V = 1.4 ℓ
Gas Collection Line
Wet Gas Meter
5.1 cm
Outflow
Recirculation Vessel
V= 5.2 ℓ
199 cm
246 cm
Filter Media
V = 54.6 ℓ
Recirculation Pump
V=2.8 ℓ
10.2 cm
Inflow
Sludge
V=3.8 ℓ
28 cm
Solids Collection

Figure 1. The Completely Mixed Anaerobic Filter

and fed from a 10 liter container into the anaerobic filter using an electrolytic gas cell, in which the O_2 and H_2 generated were used to expand a bladder located in the leachate container to displace its content. Due to the formation of iron hydroxide solids, the leachate could not be fed with regular positive displacement pumps without excessive wearing.

RESULTS AND DISCUSSION

Studies on the effectiveness of the anaerobic filter in treating high strength leachate from the lysimeter were conducted for a period of 518 days starting July 3, 1973. During Phase I of the study, which lasted 218 days the different start-up procedures and pH stabilities of the unit were tested, while in Phase II which lasted 250 days, the various operational difficulties of the completely mixed unit were evaluated. Phase III, which lasted 50 days, was used to study the effluent characteristics as affected by organic loading. A summary of the different steps is given in Table 1.

Start-up of the Anaerobic Filter

The start-up of the anaerobic filter was tested during the early stage of the Phase I study. It was noted that when the undiluted leachate was passed through the unit without seeding no significant biological degradation would occur for a 33 day period when the unit was operated at a detention time of 42 days. Also, no biomass would develop on the filter media, even when the pH of the incoming leachate was adjusted with sodium hydroxide from 5.8 to 7.0, i.e., the minimum required pH for methane fermentation. The filter was therefore emptied and the bottom section was seeded with 1 liter of digested sludge containing a total 25 g solids while the column was filled with the leachate diluted to one tenth of its strength with distilled water. Thereafter the unit was fed 1.6 liter of the diluted leachate to give a detention time of 42 days. A high initial gas production was observed which gradually decreased (Figure 2a). Increasing the influent concentration by using a lower dilution ratio resulted in increasing amounts of gas being generated in the unit as a result of the microbial methane fermentation. However, when the undiluted leachate was fed, inhibition was observed as the gas production ceased completely. A larger quantity of 2 liter of digested sludge, containing 50 g solids, and a less rapid increase in the influent concentration, however, resulted in a satisfactory gas production, approaching the theoretical amount as calculated from the COD removal

Table 1. Different Phases and Experimental Conditions During the Anaerobic Filter Study

Phase	Duration (days)	Period	Duration (days)	Hydraulic Detention Time (days)	Leachate Feeding Rate (ℓ/d)	Combined Influent Flow Rate (ℓ/d)	Recirculation Ratio	Leachate Influent COD (mg/ℓ)	Experimental Conditions
I	218	1a	1-33	42	1.6	32.4	1:20	62,000	no pH adjustment; no seeding
		1b	33-64(31)	42	1.6	32.4	1:20	62,000	pH adjustment to 7; no seeding
		2a	64-103(39)	42	1.6	32.4	1:20	6,200-62,000	seeding 1ℓ sludge; decreasing dilution
		2b	103-146(43)	42	1.6	32.4	1:20	6,200-31,000	seeding 2ℓ sludge; decreasing dilution 1:10 to 1:2
		3a	146-188(42)	42	1.6	32.4	1:20	27,000	feed 1:2 diluted leachate
		3b	188-200(12)	42/7	1.6/9.7	32.4/40.5	1:20/1:4.2	27,000	first shockload
		3c	200-218(18)	42/4.25	1.6/16	32.4/46.8	1:20/1:2.9	27,000	second shockload
II	250	1a	218-291(73)	42	1.6	32.4	1:20	27,000	start of extensive monitoring
		1b	291-293(2)	42/3.0	1.6/22.7	32.4/53.5	1:20/1:29	27,000	Third shockload
		1c	293-298(5)	42	1.6	32.4	1:20	27,000	extensive monitoring
		1d	298-362(64)	42	1.6	32.4	1:20	19,500	gradual toxicity, Na_2S
		2	362-398(36)	42	1.6	32.4	1:20	19,500	solids collection device installed
		3	398-432(35)	42	1.6	32.4	1:20	19,500	between period 2 and 3
		4	432-467(35)	74	0.9	31.7	1:35	39,000	doubling of leachate concentration
III	50	1	467-497(30)	74	0.9	31.7	1:35	32,000	kinetic analysis
		2	497-512(15)	17.5	4.0	34.8	1:8.7	32,000	kinetic analysis
		3	512-517(5)	7.5	9.1	39.9	1:4.4	32,000	kinetic analysis

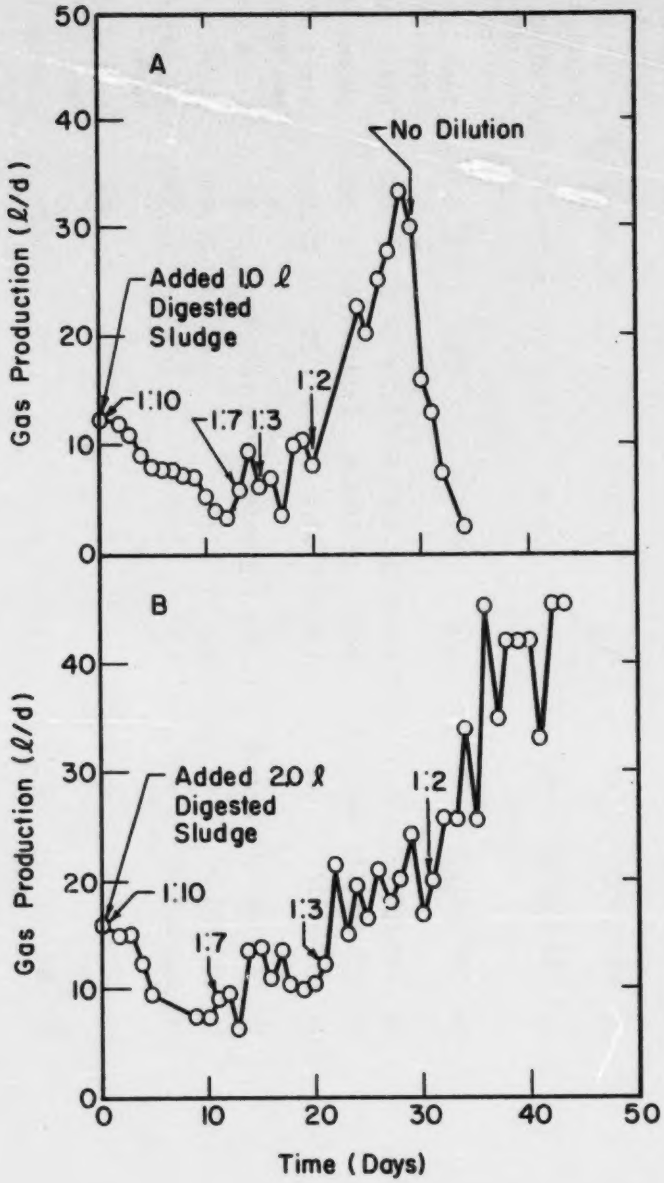

Figure 2. The Startup of the Anaerobic Filter

(Figure 2b), after 43 days. In order to prevent possible further inibition, a new batch of leachate was fed to the unit at a 1:2 dilution (1 part of feed to 1 part of dilution water) resulting in an influent COD of 27,000 mg/ℓ. Similarly to the present study Young and McCarty (1968, 1969) noted that about 40 days of operation were required to reach equilibrium conditions when two additions of 30 g volatile solids from a sludge digester were used to start the filter. Adding 30 g of digested sludge to the bottom section of an aerobic filter, Jennett and Dennis (1975) noted that only 20 days were required to reach equilibrium conditions.

Recirculation Ratio

After a 42 day operating period, equivalent to one volume turnover, the required recirculation ratio was studied. Approximately 63 percent of the constituents in the initial leachate batch would be displaced after one volume turn over for a completely mixed reactor. Initially, a 1:20 recirculation ratio was arbitrarily selected at the beginning of the study. A recirculation ratio of 1:20 was defined as 1 part of feed to 19 parts of effluent to results in a total volume of 20 parts. A titration curve of the effluent as shown in Figure 3a, indicates that the highest buffering capacity of the effluent is observed at a pH of 6.2, shile less is available at the actual effluent pH of 7.2. The pH of the inflection point at 3.9 reflects the presence of both bicarbonates and fatty acids. If only bicarbonate had been present, the pH of the inflection point would have been close to 4.3. Because of this observed shape of the effluent titration curve, five parts of effluent are required to increase the pH of the influent to 7.0, thus, requiring a minimum ratio of 1:6 (Figure 3b). In order to operate the unit safely and well-mixed the ratio of 1:20 was maintained by using a recirculation flow rate of 30.8 ℓ/d, resulting in a complete mixing of the unit every 1.8 days as calculated for the column volume subject to mixing. Since the time required for mixing was short as compared to the hydraulic detention time, i.e., 1.8 days versus 42 days, the unit can be considered completely mixed. As a result of the recirculation, the vertical upflow rate in the unit was 1.1 m/d.

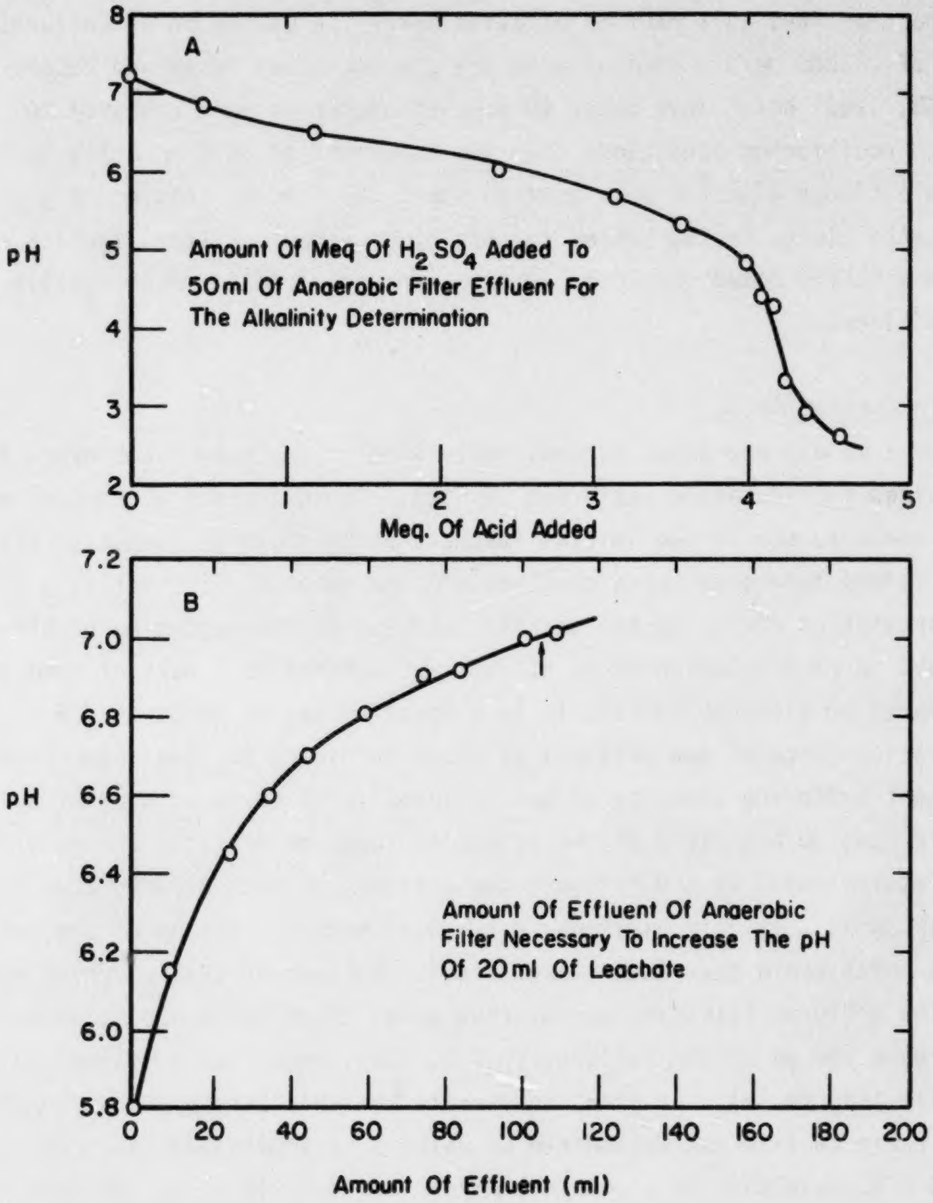

Figure 3. Determination of the Minimum Required Recirculation Ratio

Shockloading

Before a more extensive monitoring was initiated, the ability of the anaerobic filter to withstand shockloads was studied. When the detention time, based on feed stream flow alone, was reduced from 42 days to 7 days for a one-day period, only a small change in the pH was observed (Figure 4a and b). Since the recirculation flowrate was kept constant, the recirculation ratio experienced a decrease. The pH decreased to 6.9 when the detention time was reduced to 4.25 days for a one-day period (Figure 4c and d). A larger shockload was conducted in Phase II, 73 days after the more intensive monitoring of the unit had started. The detention time was reduced to 3 days for a two day duration which also caused a similar lowering of pH values (Figure 4e and f). The gas production did not show a corresponding increase, as high concentration of organics were present in the effluent of the unit (Figure 5a) which reduced the organic removal efficiency to 54 percent. The high COD values corresponded with high concentrations of fatty acids (Figure 5b), aromatic hydroxyls and carbohydrates (Figure 6a). The large differences in the values for the filtered and unfiltered COD may indicate that substantial quantities of solids were resuspended at the higher flow rates. This was also indicated by the suspended solids (SS) analysis (Figure 7b). As most of the phosphates in the unit are present as suspended solids, a similar pattern as the SS was observed (Figure 7c). Since fatty acids contribute to the alkalinity, an increase parallel to the fatty acids was observed (Figure 7e). After the detention time was restored back to 42 days after the two days shockload, the effluent COD and SS concentrations returned to values only slightly higher than those observed before the shockload. It is realized that at short detention times the flow regime of the unit tends to depart from a completely mixed pattern and approaches that of a plugflow, since at a three day detention time, the content is only mixed 2.7 times during one volume turnover. Based on these tests it was concluded that the buffer capacity of the unit is sufficient to prevent large pH depressions at relatively short detention times. However, at detention times as short as three days a large portion of the organics leave the unit in the effluent stream. Further-

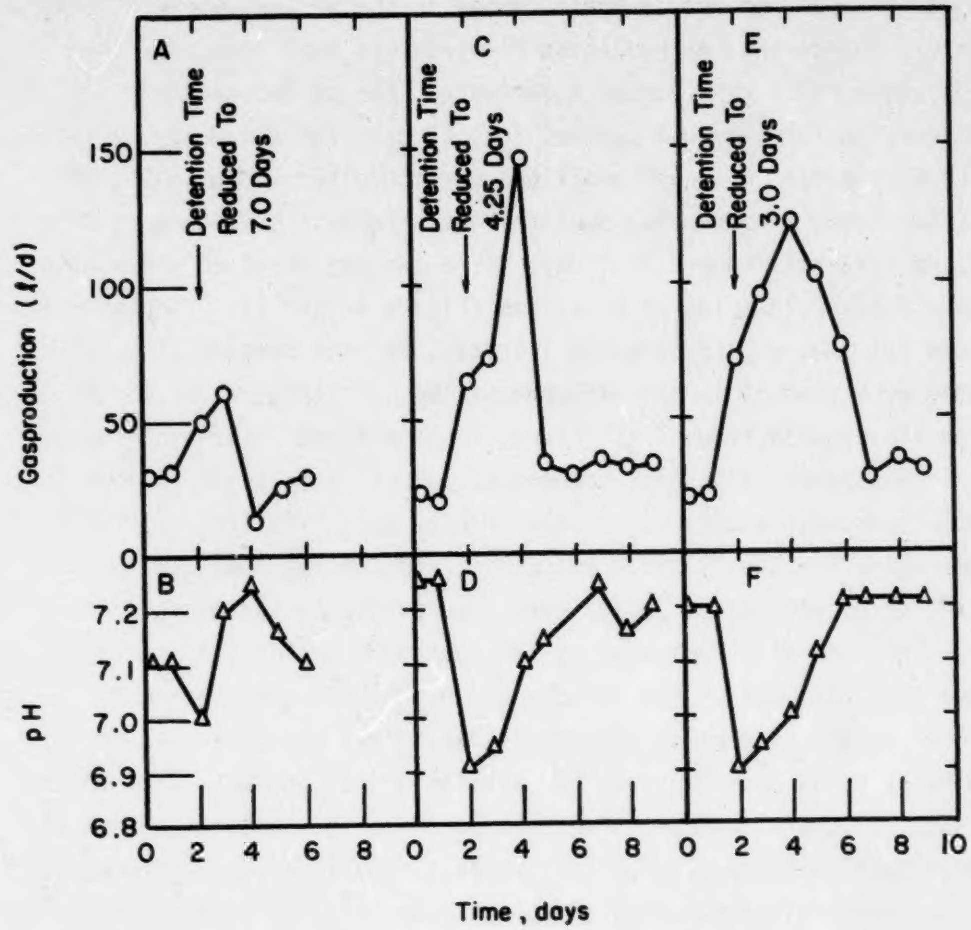

Figure 4. Stability of the Anaerobic System under Different Shockloads

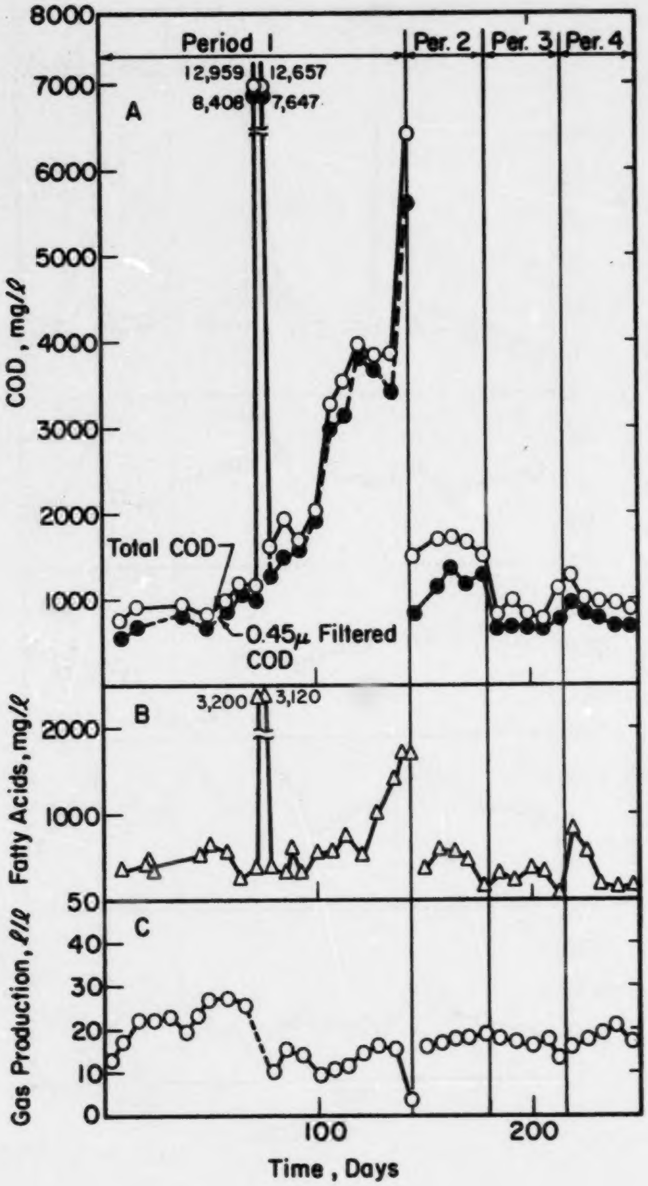

Figure 5. Effluent Quality During Phase II as Measured by COD, Fatty Acids and Gas Production

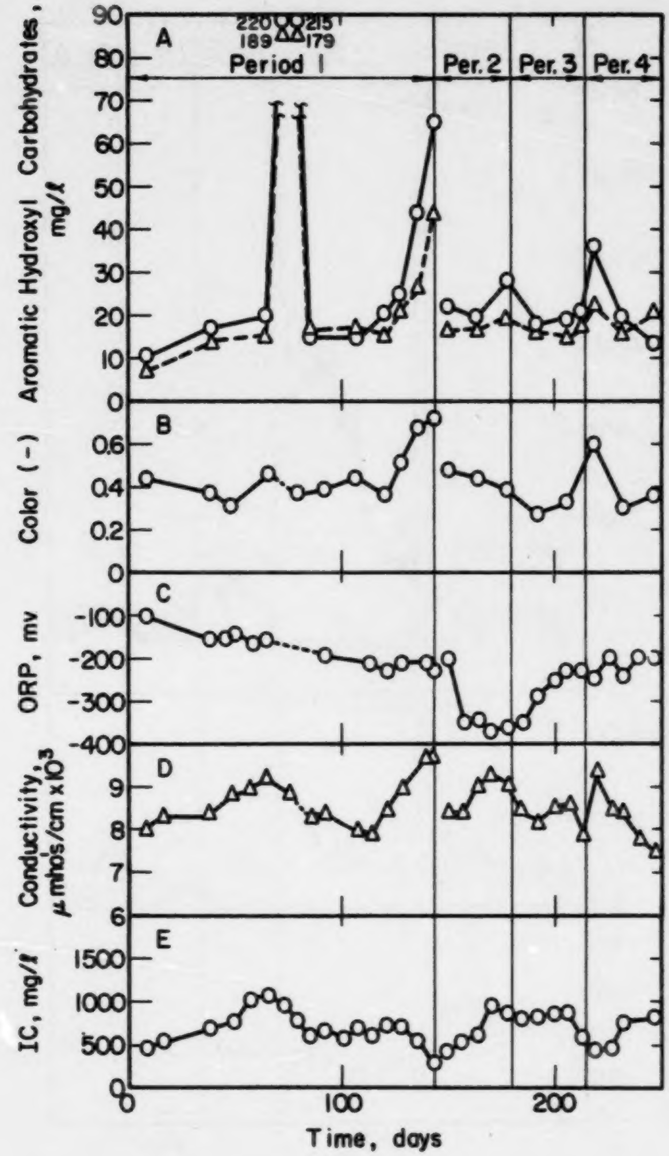

Figure 6. Effluent Quality During Phase II as Measured by Carbohydrates, Aromatic Hydroxyls, Color, ORP, Conductivity and Inorganic Carbon

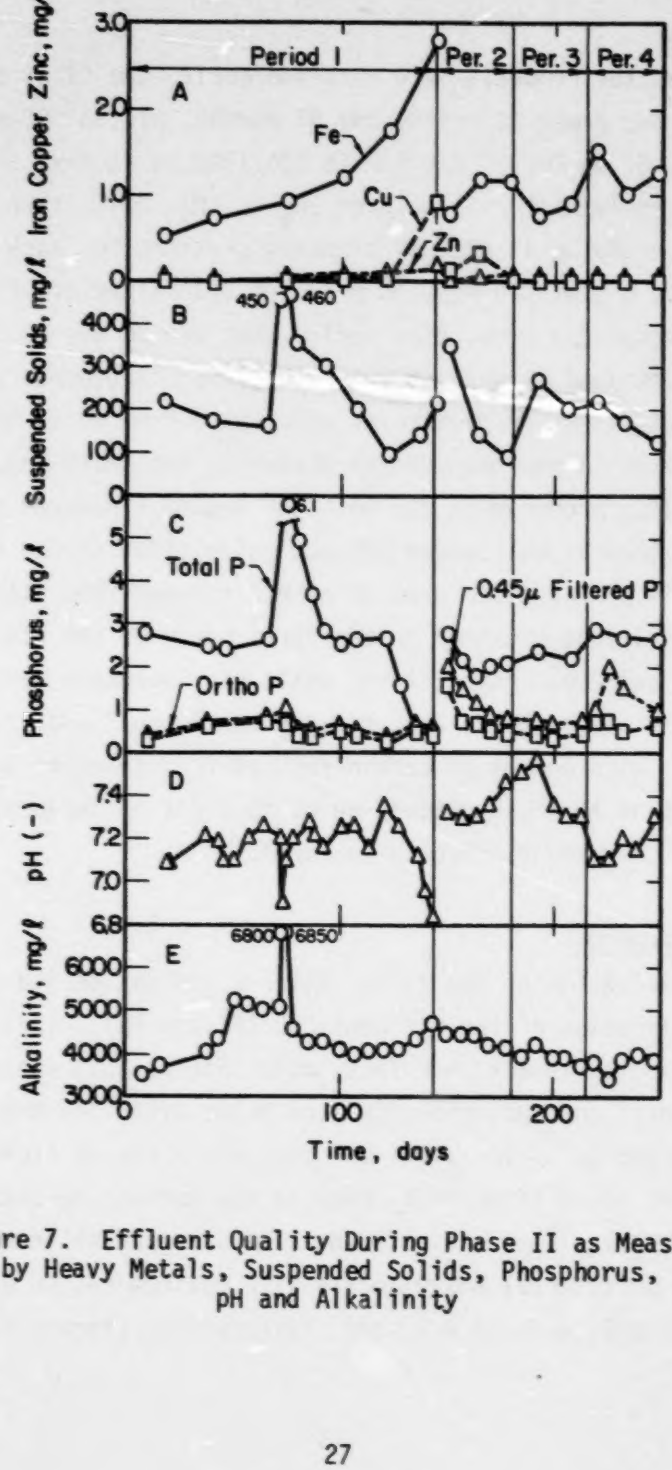

Figure 7. Effluent Quality During Phase II as Measured by Heavy Metals, Suspended Solids, Phosphorus, pH and Alkalinity

more high concentration of suspended solids are detected in the effluent at such short detention times.

Gas Production

High organic matter removals were observed during the first 60 days of monitoring in the Phase II period and 97 percent of the COD was removed at a rate of 0.62 kg COD/m^3 day (39 lb COD/1000 cu ft day) (Figure 5a). As the oxygen equivalent of 1 mole of CH_4 is $2O_2$, 22.4 liter of methane are therefore produced at 0°C and standard pressure for each 64.4 g COD removed. Thus, 1 g of COD removed produces 0.38 liter of methane gas at 25°C. The average gas production during that period was 23.3 ℓ/ℓ influent, and the gas contained 78 percent methane. This corresponds to 89 percent of the theoretical gas production as calculated from total COD removals. The difference of 11 percent was attributed to the small amount of biological solids produced in the unit and organics removed by physical processes. A theoretical carbon balance calculation showed that 1.75 liter of gas is produced per gram of carbon removed from solution. The leachate and effluent obtained in the first phase of the study had COD/TOC ratios of 3.5 and 2.8, respectivley, while the inorganic carbon concentration present in the influent and effluent was 10 mg/ℓ and 750 mg/ℓ, respectively. This amount of carbon removed from solution would theoretically correspond to a gas production of 23.2 ℓ/ℓ of influent which was 99 percent of the amount actually measured.

Heavy Metal Toxicity

Continuing observation of the filter after a 100 day period showed a gradual deterioration of the effluent COD (Figure 5a). This was subsequently reflected in a higher fatty acid (Figure 5b), carbohydrate and aromatic hydroxyl concentrations (Figure 6a). After 144 days, the COD removal decreased to as low as 64 percent, while the pH decreased below 6.8 (Figure 7d) which effectively reduced the methane fermentation (Figure 5c). Analysis of the effluent showed a gradual increase in soluble (0.45 μ filtered) heavy metals with maximum Fe, Cu and Zn concentrations of 2.8, 0.9 and 0.2 mg/ℓ, respectively (Figure 7a), indicating that heavy metal toxicity may have inhibited the anaerobic fermentation. The metals were mostly present in the suspended form and the dissolved iron, for example, represented only 9 percent of the total iron content.

Lawrence and McCarty (1965) and Mosey *et al.* (1971) showed that the concentration of soluble heavy metals was determined by the amount of sulfide present in the unit to form insoluble sulfide precipitates. Since iron is the metal generally present in highest concentrations, the ferrous sulfides in the unit constitute a sulfide reservoir to precipitate the more toxic and less soluble heavy metals such as copper, zinc and nickel. Based on the measurement of soluble sulfides in digesters, Mosey and Hughes (1975) concluded that a 50 percent decrease in gas production would occur at concentrations of 10^{-4} mg/ℓ Zn^{++}, 10^{-7} mg/ℓ Cd^{++}, 10^{-12} mg/ℓ Cu^{+} and 10^{-16} mg/ℓ Cu^{++}. Inhibition during shockloads of short duration occurs at much higher soluble heavy metal concentrations of 0.5 mg/ℓ Zn^{++}, 1 mg/ℓ Cd^{++}, 10^{-7} mg/ℓ Cu^{+} and 10^{-8} mg/ℓ Cu^{++}. Kirsch and Sykes (1971) reported that at a total zinc concentration of 100 mg/ℓ and a soluble concentration of 1.5 mg/ℓ, gas production was inhibited. However, failure did not occur when the zinc was fed as zinc sulfate as a result of which the soluble zinc concentration never exceed 0.4 mg/ℓ. None of the studies noted a toxicity due to iron.

Since the present study noted significant concentration of copper, one of the most toxic elements, the observed inhibition could well be due to this element. Similar to Lawrence and McCarty (1965) it was noted that the initial deterioration of the effluent COD was not caused by a higher fatty acid concentration, indicating that the acid fermenting bacteria were more affected by the inhibiting substance than the methane bacteria. A limited number of analyses indicated that approximately half of the sulfate concentration of 550 mg/ℓ, in the 1:2 diluted leachate was removed in the unit by reduction and precipitation. Stoichometric amounts of sulfide would only precipitate 9 percent of the iron removed in the unit, indicating that the majority of the iron at neutral pH values would be precipitated as carbonates and hydroxides; a conclusion similar to that reached by Mosey and Hughes (1975). Unlike the metal-sulfide precipitates, the carbonate precipitates are very pH sensitive and dissolve at low pH values. This may explain the increase in Zn and Cu concentrations between 120 and 144 days (Figure 7a). These results may indicate that initially the acid fermenting bacteria were partially inhibited by metals resulting in higher effluent COD (Figure 6a). This was subsequently followed by inhibition of the methane bacteria, as a result of which the fatty acid concentration gradually increased (Figure 5b). Since less bicarbonate alkalinity was formed, the pH in the unit started to decrease, which in turn dissolved additional heavy metal precipitates; the solubilized metals when resulted in further inhibition. The results further show that the values of pH and conductivity reflect increases in the fatty acid concentration. The earliest warning of possible metal toxicity, however, is given by a gradual decrease in total gas production and an increase of the effluent COD. To reduce the observed toxicity half of the column volume was drained and filled with tap water to reduce the inhibiting substances. Since metal toxicity was suspended, their concentration was decreased by addition of 75 mg/ℓ Na_2S to the column content, while a similar concentration was added to the influent for the next 18 days. After these operational changes the observed effluent quality during the second monitoring period of Phase II improved greatly while the gas production, the organic matter removal, and the bicarbonate alkalinity increased gradually. The sulfide additions caused a decrease in ORP values while reducing the heavy metal concentrations (Figure 6c). Furthermore, no H_2S odor was detected also indicating that the toxicity was caused by metals.

In subsequent studies with the same anaerobic filter using a different feed, experiments were made to study the effect of hydraulic loading on the removal of heavy metals. Four different loadings were evaluated in duplicate during which the metal concentrations in samples withdrawn from the different sampling ports along the filter were measured. Using the effluent and influent concentrations, the removal percentages can be calculated. The analytical results in Figure 8 show that the removal of most metals is 68 percent or higher, except for copper and cadmium. The

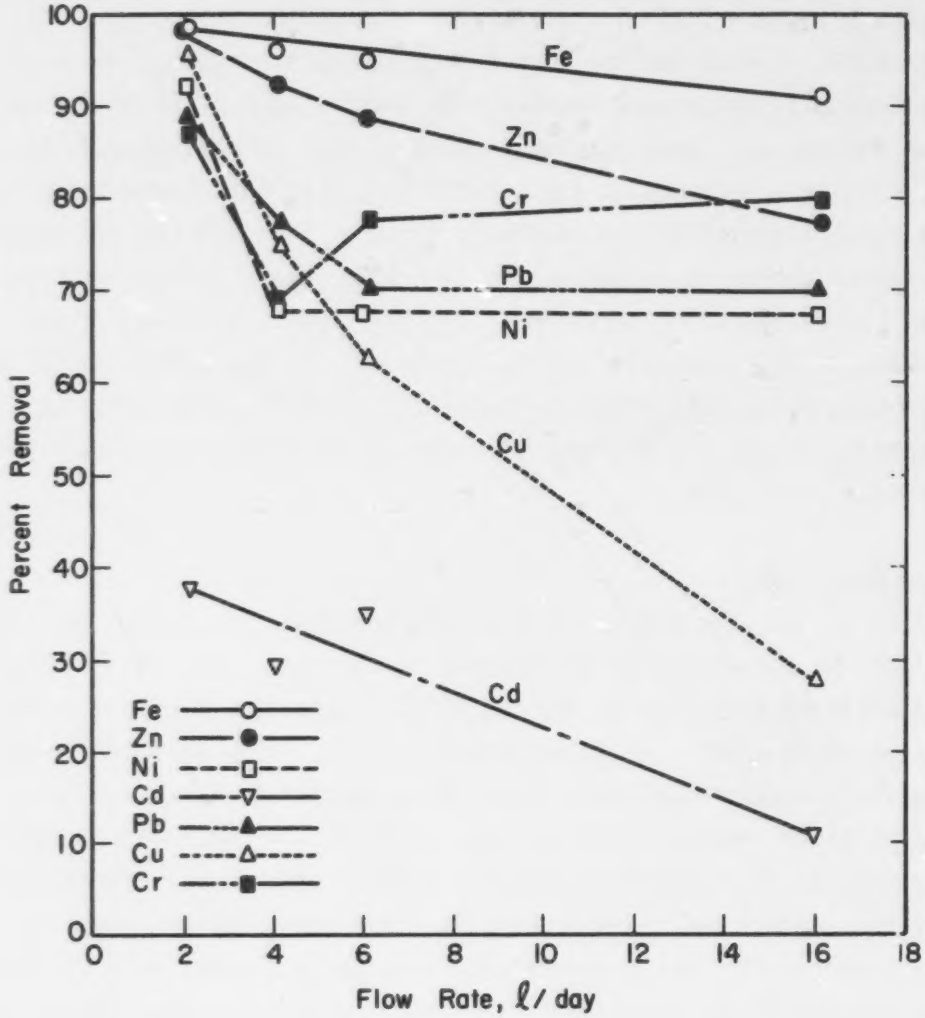

Figure 8. Effect of Increasing Hydraulic Loadings on Percentage Removal of Different Heavy Metals

percentage removal generally decreases with increasing flowrates with the exception of chromium, which element is likely present as the chromate anion and not as the cation. Iron showed the highest removals while it also had the highest initial concentrations. Cadmium had the lowest removals while it also had the lowest initial concentration. The most rapid decrease in percentage removal with increasing feed flowrates was observed for copper. Thus at high loadings copper is removed to a lesser extent than the other metals, again indicating that this element may cause a metal toxicity in the anaerobic filter. Although the percentage metal removal decreases at increasing flowrates, the absolute quantity of metals increases with increasing flowrates. Since a large portion of the metals form insoluble sulfide, carbonate and hydroxide precipitates, which coagulate and settle out in the unit, increased metal concentrations were observed in the sludge drawn from the bottom portion of the filter (Figure 9).

Nutrient Requirements

Comparison of effluent and influent total phosphorus (P) showed that 55 percent of the concentration was removed in the unit. The COD:P ratio of the influent, however, was as high as 4360:1 indicating that a phosphorus limitation could occur. Young and McCarty (1968, 1969) selected a 470:1 ratio using a protein-carbonate waste and a fatty acid waste. McCarty and Speece (1963) measured that a feed COD:P ratio of as high as 2200:1 was feasible in an anaerobic digester fed with fatty acids. Foree and Lovan (1971) maintained a 500:1 ratio in their unit treating press brewery liquor. The latter investigators noted that about half of the applied phosphorus was utilized in the unit. In a subsequent investigation using the same unit they maintained a COD:P ratio of 1000:1 using a wastestream similar to the one used in the present study (Foree and Reid, 1973). They noted that 96 percent of the applied phosphorus was removed, indicating that only slightly higher ratios are feasible. Although the waste in the present study was fed to the units without nutrient supplements, a significant amount of phosphorus of 1328 mg was initially introduced in the unit through the anaerobic sludge used to feed the unit.

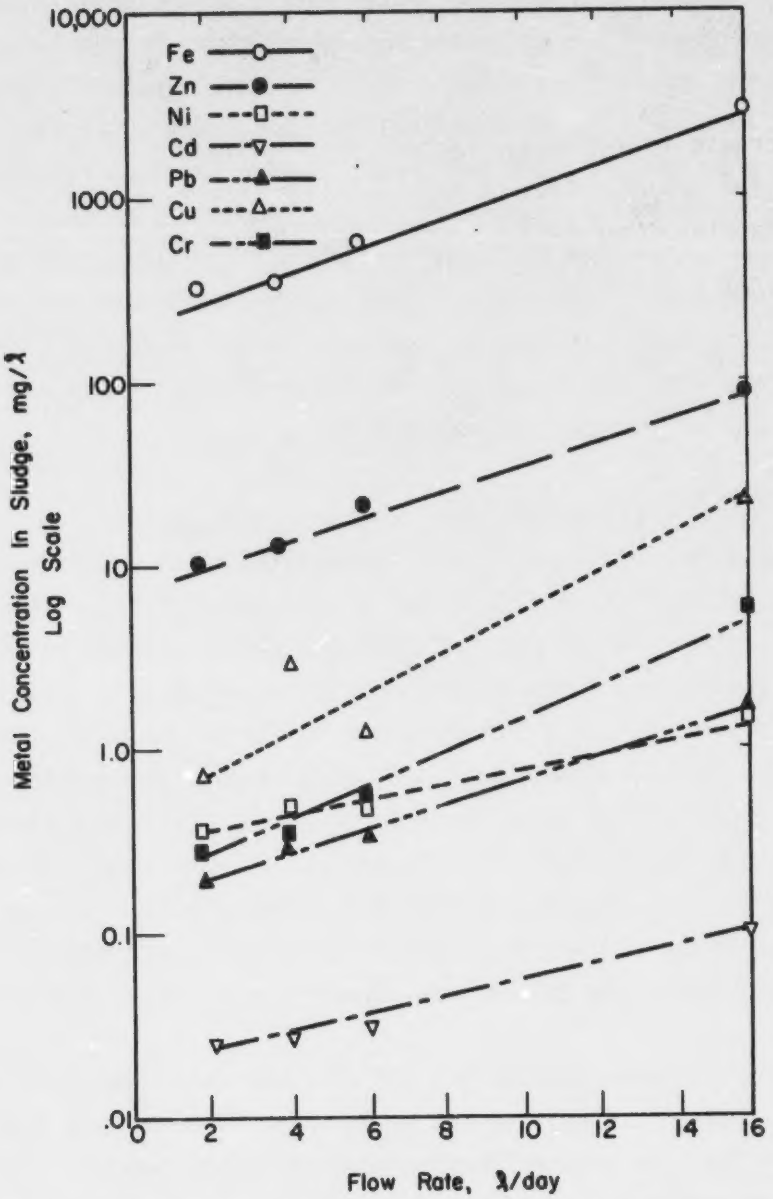

Figure 9. Effect of Increasing Hydraulic Loadings on the Metal Concentration in the Sludge Collected from the Bottom of the Anaerobic Filter

The COD:P ratio of 4360:1 should therefore be considered as an upper limit. The COD:N ratio of the feed was 39:1 indicating that no nitrogen limitation would occur. When the phosphates were distinguished in total, soluble and orthophosphates, it was noted that about three fourths was present in the suspended solids form (Figure 7c). The total phosphate concentration, therefore parallels the suspended solids measurements, as observed during the evaluation of the third shockload. During the toxicity period a significant decrease was observed in total phosphate concentration, probably as a result of the formation of metal phosphate precipitates. After addition of 75 mg/ℓ Na_2S, higher soluble phosphate concentrations were observed, possibly because less metals were available to form precipitates with the phosphates; the total effluent P concentration, however, did not change substantially.

Factors Affecting Effluent Organic Matter Concentrations

It was noted that after addition of the sulfides, the differences between total COD and the COD in filtration of 0.45 μm Millipore filter became more substantial. As it was felt that the higher organic solids content could be due to insufficient settling within the unit, a solids collection compartment of 3.8 liter was added to the column below the influent inlet compartment (Figure 1). Visual observations showed that solids were collected in this compartment to gradually build up a sludge slurry. Comparison of the effluent data showed both a lower total COD and soluble COD in period 3 as compared to period 2 probably as a result of the solids collection device (Figure 5a). The differences in suspended solids concentration between the two periods, however, were not noticeable.

In order to determine whether the effluent concentration is solely determined by organic loading, and not by influent concentration and hydraulic detention time, the organic loading was maintained constant, while the influent concentration was doubled, by feeding the unit with undiluted leachate instead of the 1:2 diluted leachate. Simultaneously the detention time was doubled to maintain the constant loading. The results in Figure 5, 6 and 7 indicate a temporary deteriorating effluent quality of

COD, fatty acids and carbohydrates. Both pH and bicarbonate alkalinity decreased during this period but returned to initial values after a 15-day period. After this initial adaption, effluent qualities were generally similar for period 3 and 4, indicating that the influent concentration does not affect the effluent quality under the conditions studied; however, it does affect the percentage of COD removal. Similar conclusion was reached by Young and McCarty (1968, 1969). They noted that when the organic loading was maintained while both the influent concentration and the hydraulic detention time were decreased, the unit gave a constant percentage COD removal at low loadings but a decreasing percentage at high loadings. Jennett and Dennis (1975) found that at a constant removal rate of 3.5 kg COD/m^3 day (220 lb COD/1000 cu ft day) the percentage removal decreased from 98 percent to 95 percent and 94 percent respectively, when the influent concentration decreased from 16,000 mg/ℓ, 8000 mg/ℓ and 4000 mg/ℓ. Contrary to the results in the present study, they also noted that the actual effluent concentration decreased. Based on these results one would conclude that recirculation does not affect the effluent quality as the latter is only determined by the substrate removal rate. Recirculation, however, is necessary to maintain sufficient high pH values to treat the acidic feed. A completely mixed regime would allow utilization of the entire length of the column for substrate removal; in plug flow units, however, only the lower one meter (3.3 ft) is effective (Young and McCarty 1968, 1969; Jennett and Dennis, 1975). As such, increasing the height of the completely mixed unit with respect to the area at the base will reduce the total column requirement for the same degree of treatment and, therefore, lower construction costs (Germain, 1964).

Effect of Removal Rate on Organic Matter

Since the effluent organic matter concentration is mainly determined by the substrate removal rate of the unit and not by influent concentration or hydraulic detention time, the third phase of the study was conducted to establish such relationships. During the initial 30 days of the third phase, the detention time was similar to the fourth period of the second phase, i.e. 74 days. Although slightly less than one volume turn-over was realized, analysis of the effluent quality indicated that steady state operations were realized (Figure 10 and 11).

When the detention time of the unit was reduced to 17.5 days, higher effluent concentrations were generally observed (Figure 10 and 11). An increase was observed for both the biodegradable fatty acids and for the less readily degradable carbohydrates and aromatic hydroxyls. Reduction of the detention time to 7.5 days caused a further increase in organic matter concentration in the effluent. As the quantity of available leachate was limited, only a 0.7 volume turnover was realized at this loading. The effluent parameters, with exception of the carbohydrates, however, indicated that steady-state operations were obtained. Both pH and inorganic carbon concentrations showed that the unit was effectively operating at this detention time. The phosphate analyses also indicate that this nutritional element is not limiting the biological growth at higher rates of substrate removal. Although a larger amount of organic matter is removed at the higher loading, the resulting higher organic matter content in the effluent is a major disadvantage. A material balance during Phase III indicated that 93 percent of the COD could be accounted for by the methane gas leaving the unit. The effluent concentration generally reached new equilibrium levels after about 2 days after a change in the loading. Young and McCarty (1968, 1969) similarly noted that when the loading to the anaerobic filter was increased, the gas production rate increased within two days. Jennett and Dennis (1975) found that immediately after a loading change the effluent COD concentration increased temporarily but returned to new steady-state levels after about 10 days. They also noted that the temporary increase in effluent COD was more noticeable when the loading increase resulted from a higher influent concentration than from a decrease in detention time. This tends to agree with the results obtained in this study.

Although the actual effluent concentration is determined by the rate of substrate removal, the percentage of removal, however, is determined by the hydraulic detention time. The removal percentage for the completely

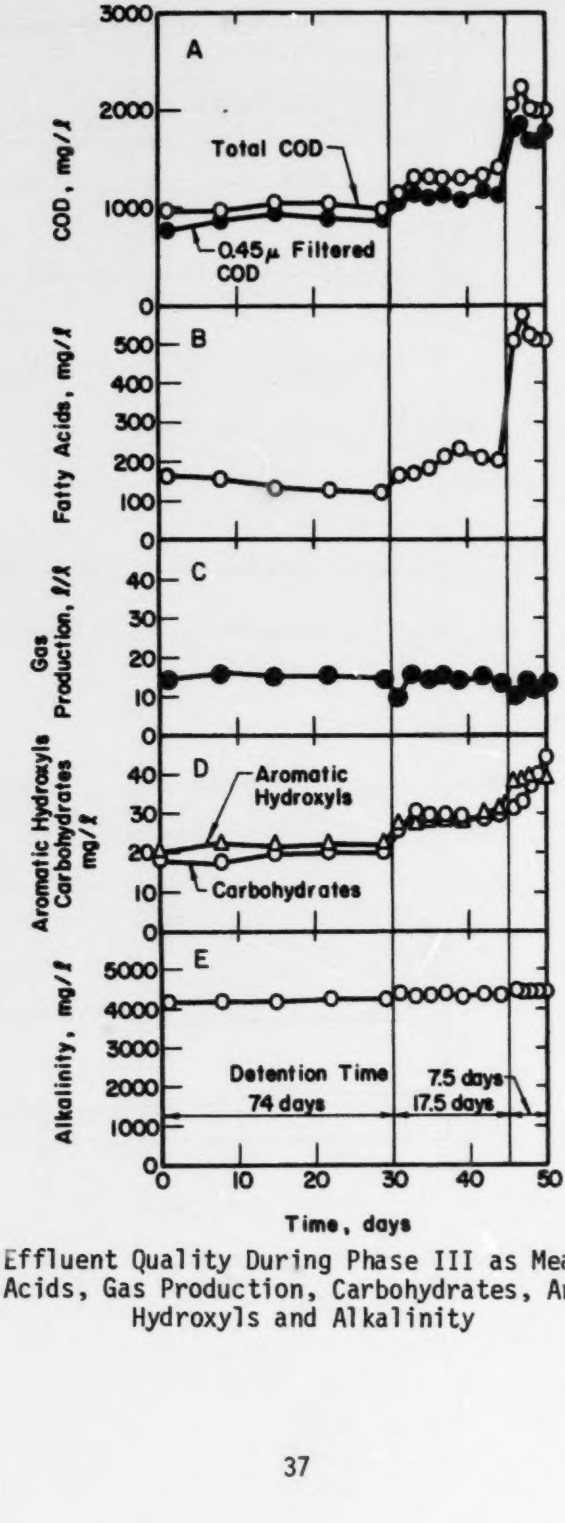

Figure 10. Effluent Quality During Phase III as Measured by COD, Fatty Acids, Gas Production, Carbohydrates, Aromatic Hydroxyls and Alkalinity

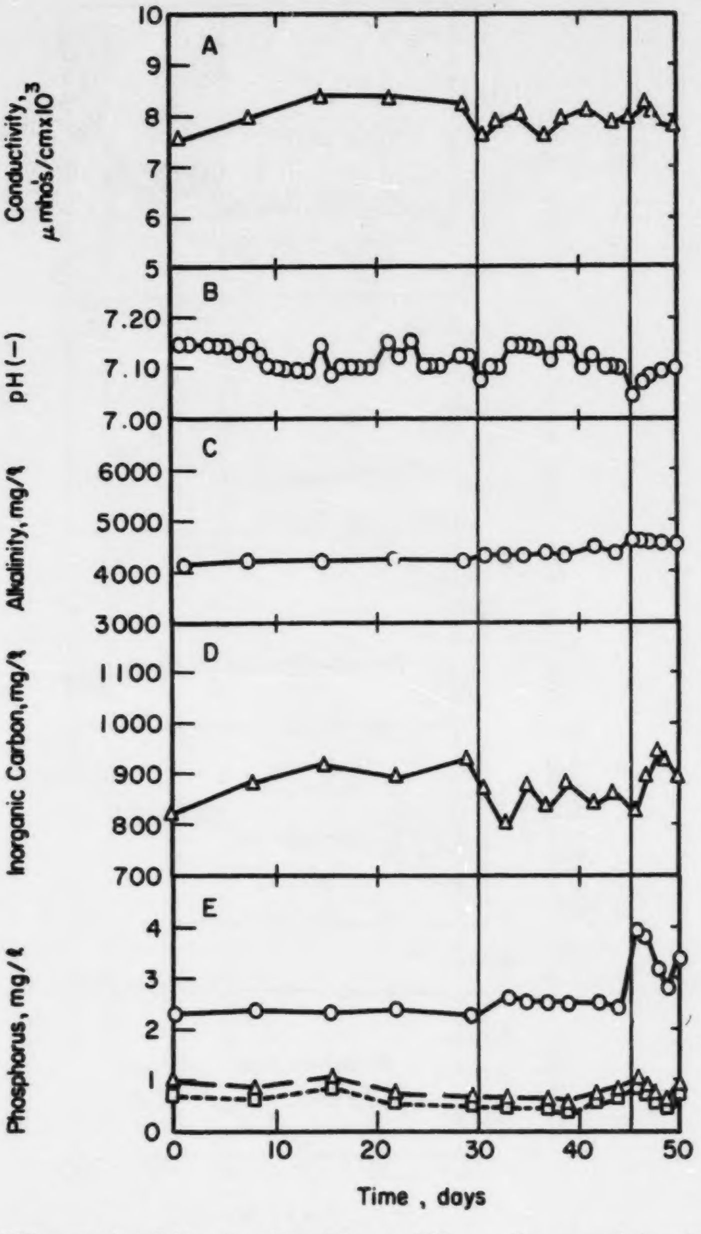

Figure 11. Effluent Quality During Phase III as Measured by Conductivity, pH, Alkalinity, Inorganic Carbon and Phosphorus

mixed unit was therefore calculated during the three detention times of 74, 17.5 and 7.4 days in Phase III and the 3 day detention time during the shockloading in Phase II (Figure 12). In addition, the percentage removal as predicted for plugflow units by Young and McCarty (1968, 1969) is shown for comparison. They formulate that the efficiency was inversely related to the hydraulic detention time. The results of the two systems indicate that at long and short detention times reasonable agreement is observed. At intermediate ranges, however, the observed results showed higher percentages of removal for the unit in the present study. The data also indicate that the unit should be operated above a detention time of 7 days in order to obtain more than 95 percent COD removal.

At the end of the third phase, tap water was introduced in the unit to study whether the mixing regime as a result of the recirculation agreed with the completely mixed model. The results of the color dilute-out clearly indicate that this is still true after accumulation of appreciable amount of biomass, since 63.2 percent is removed after one volume turnover (Figure 13a). The initial section of the total P curve (Figure 13b) shows an identical result, but shows higher removals after about one volume turnover, possibly as a result of precipitation under the more aerobic conditions resulting from the tap water additions. The suspended solids show the highest decrease since their removal is also aided by sedimentation. A lower dilute-out is observed after about 70 percent of the suspended solids are removed indicating that the remaining fraction consists of smaller particles.

Effluent Organic Matter Composition

An evaluation of the relative compositions of the effluent organic matter at the three loadings is shown in Figure 14. The fourth data point was obtained during Phase I when the unit was subject to a shockload in which the retention time was reduced to three days for a two day duration. The results in Figure 14 show that with increasing loadings a larger percentage of the organic matter consisted of free volatile fatty acids (Figure 14)

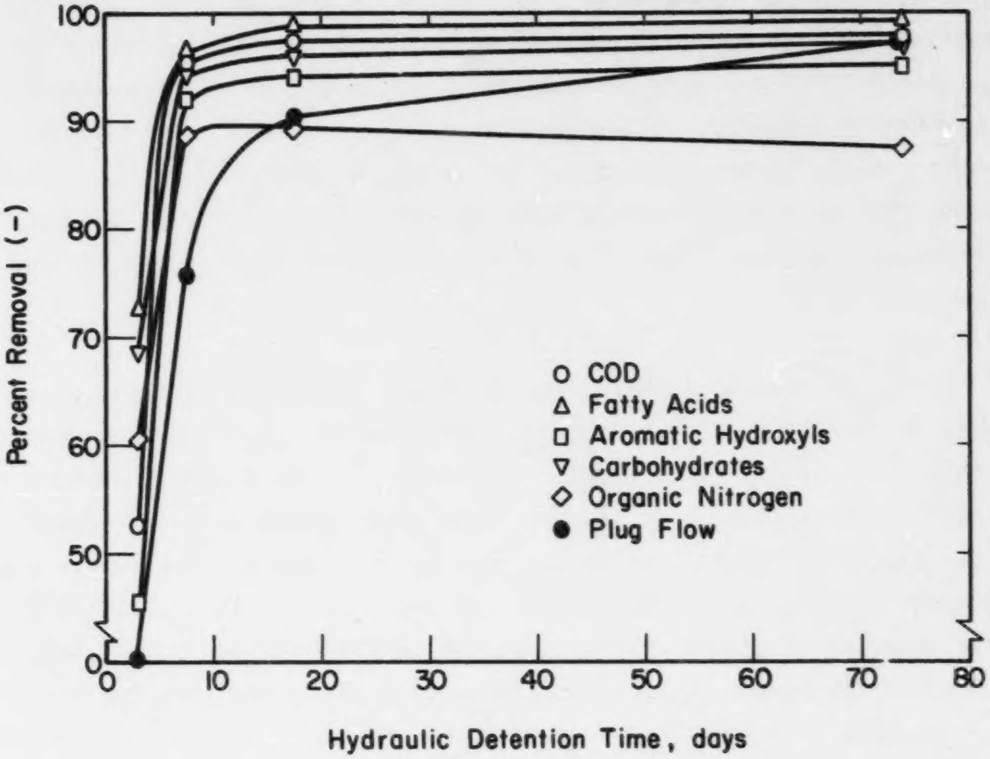

Figure 12. Percentage Organic Matter Removal at Different Detention Times

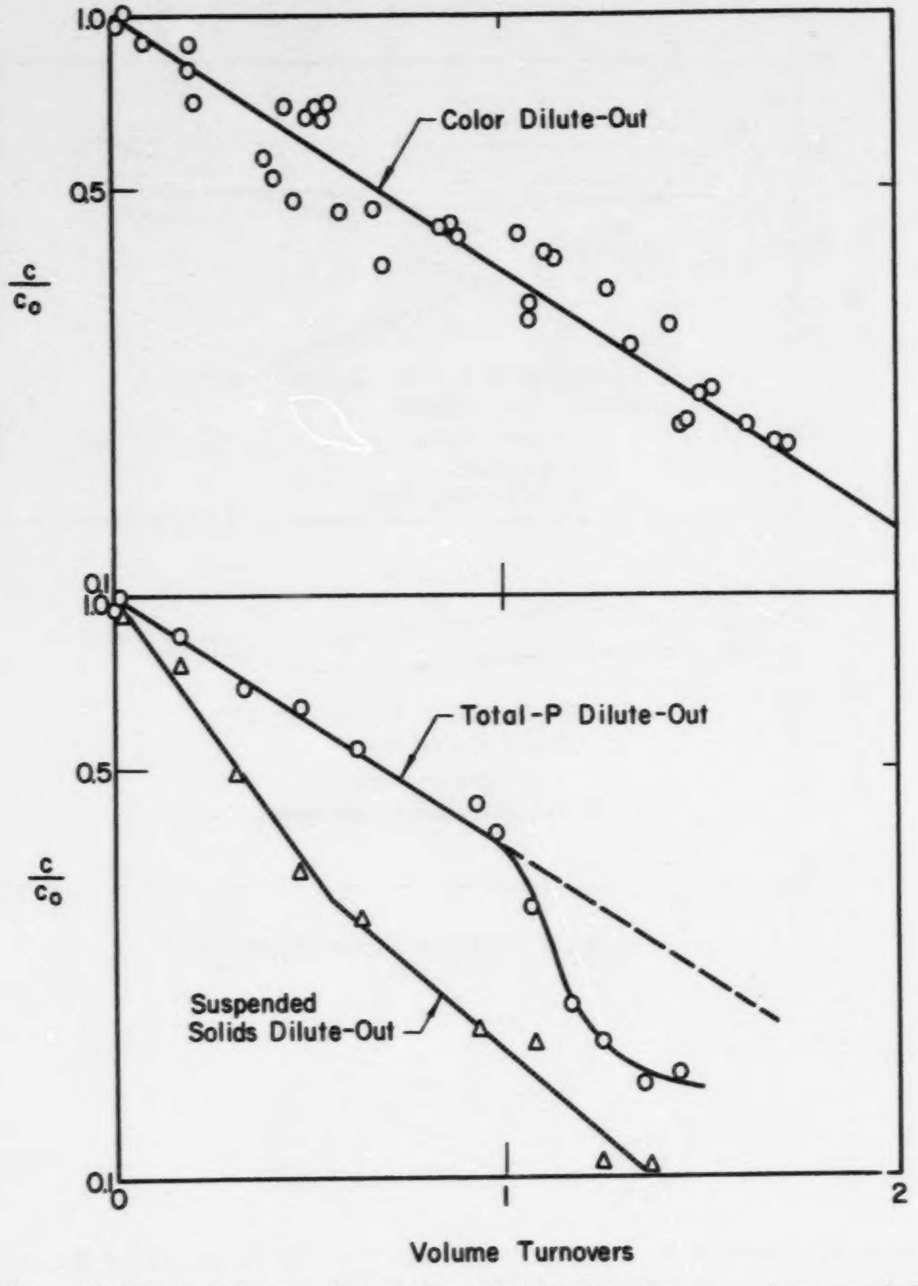

Figure 13. Dilute-Out Curves for Color, Total Phosphorus and Suspended Solids

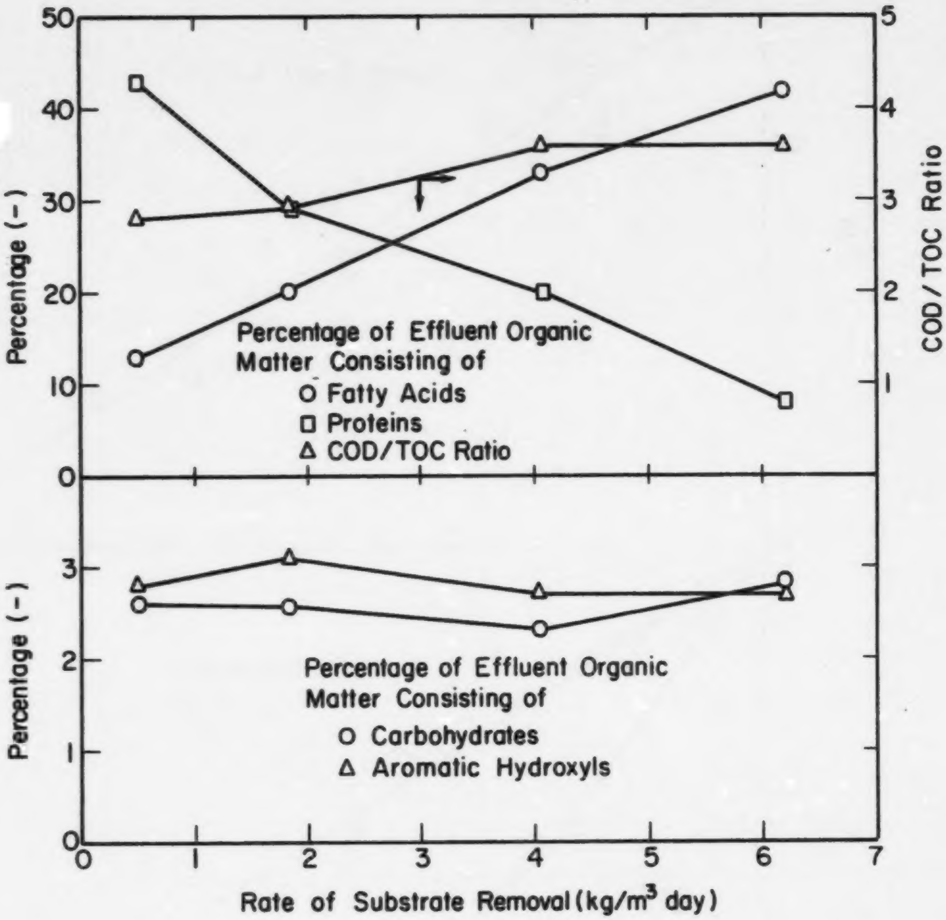

Figure 14. Effect of Rate of Substrate Removal on Relative Organic Matter Composition of the Effluent

assuming a COD/weight ratio of 1.07. This would indicate that the methane fermenting bacteria are determining the overall substrate removal rates. Young and McCarty (1968, 1969) also observed that at low loadings the percentage fatty acids decreased with decreasing loadings. However, at removal rates about 1.5 kg COD/m^3 day (94 lb COD/1000 cu ft day) the percentage fatty acids decreased with increasing removal rates, possibly indicating that at this rate the acid fermenting bacteria also become limiting. A similar optimum at 1 kg COD/m^3·day (63 lb COD/1000 cu ft day) was obtained with data from Jennett and Dennis (1975); Plummer *et al.* (1968) also observed a decreasing percentage fatty acids with increasing removal rates above a removal rate of 1.5 kg/m^3·day. A lower optimum was of 0.2 kg COD/m^3 day was calculated from data of Arora *et al.* (1975). This lower optimum may have been due to the less degradable nature of the substrate as reflected by the low BOD/COD of 0.52. The data, however, indicate that the above mentioned optimum corresponds to a substrate removal rate between 1 and 1.5 kg COD/m^3·day. The absence of such optimum in the present study is due to the fact that fatty acids are already present in the influent stream. The decrease of the percentage fatty acids at decreasing removal rates is reflected by a decrease of the COD/TOC ratio's in the effluent, indicating an increase of the oxidation state of the organic (Figure 14a).

The trend observed for the fatty acids is opposite that of the nitrogenous organics assuming a COD/N ratio of 10. The highest actual concentration was obtained at the high loading, which decreased at the intermediate loading and showed a slight increase at low loadings; the soluble COD showed a continuous decrease resulting in a gradual increasing percentage nitrogenous organics. This trend is in agreement with studies by Chian and DeWalle (1975) who noted an increase in amino acids and nitrogenous organics after removal of the free volatile fatty acids using an aerobic system. The data in Figure 14a would indicate that a similar trend is occurring in anaerobic systems. DeWalle and Chian (1974) noted a substantial increase of high molecular weight carbohydrates after removal of both fatty acids and amino acids. The absence of such increase in the present study (Figure 14b) is probably due to the low bacterial growth rates which are characteristic of anaerobic systems. This was confirmed in further tests in which the effluent of the anaerobic filter was subsequently treated in an aerated lagoon; after the fatty acids were removed a substantial increase in high molecular weight carbohydrates was observed.

Sludge Production

A solids balance was made during the third phase of the study. For this purpose any solids accummulated in the bottom section were removed prior to Phase III. At the end of the fifty-day period, sufficient solids were accummulated in the bottom section. A total of 2.5 liters of sludge were removed. The sludge had a density of 1.026 g/cm^3 and contained 3.86 percent solids with a volatile solids/total solids ratio of 0.377 to give a total of 37.3 g volatile solids. The solids density in the present study is less than observed by Arora *et al*. (1975) who obtained an 8 percent slurry with a volatile solids/total solids ratio of 0.34, but more than the 2.3 percent observed by Jennett and Dennis (1975). The calculated average concentration of volatile suspended solids in the effluent samples was 106 mg/ℓ. As 20 mg/ℓ was present in the influent the net accummulation of suspended solids during the fifty-day period was 11.2 g. Thus, about 67 percent of the recoverable solids generated in the unit will accumulate in the bottom section and can be removed by subsequent discharge to sludge drying beds; 33 percent of the recoverable solids were present in the effluent of the unit. During the fifty-day period a total of 3992 g of COD was removed, resulting in an apparent net synthesis of 0.012 g VSS formed/g COD removed. A higher yield would have been obtained if the accumulation of biological solids onto the plastic media slabs had been measured. The present value compares favorably with data calculated by Young and McCarty (1968, 1969) who observed a net synthesis of 0.015 g VSS/g COD for fatty acid waste and 0.118 g VSS/g COD for a protein-carbohydrate mixture. Jennett and Dennis (1975) using a pharmaceutical waste consisting mainly of methanol, observed a yield of 0.027 g VSS/g COD. The former included in their calculation the solids that were attached to the filter media, while the latter measured the solids that were loosely attached to the media and could be removed through the sampling ports. Assuming a VSS/P in the synthesized sludge of 60:1 (McCarty and Speece, 1963), the maximum COD"P ratio in the feed should be 5000:1 based on an apparent net synthesis of 0.012 g VSS formed/g COD removed. This ratio is comparable to that actually measured in the influent stream.

Several factors have been recognized to determine the amount of solids leaving the anaerobic filter. Young and McCarty (1968, 1969), observed a gradual accumulation of solids in the anaerobic filter during which period the effluent suspended solids remained low. Only after the filter reached its maximum storage capacity would the effluent solids show an increase. More than 70 percent of the solids synthesized within the filter can be retained in the filter when treating a fatty acid waste. However, with substrates that result in higher yields such as protein-carbohydrate wastes only 30 percent may be retained (Young and McCarty, 1968, 1969). When the influent waste contains solids, no net removal may be observed (Jennett and Dennis, 1975). Both Plummer *et al.* (1968) and Jennett and Dennis (1975) observed that the solids concentration was mainly determined by the hydraulic detention times. The present data are in agreement with both studies (Figure 7b). In addition, it is noted that the porosity of the filter may have a large effect on the solids concentration which is to be expected since a lower void ratio will increase the collision frequency between the solids and the filter media. The suspended solids, for example, were only 10 mg/ℓ at a void ratio of 0.42 (Young and McCarty, 1968), 34 mg/ℓ at a void ratio of 0.47 (Jennett and Dennis, 1975), 40 mg/ℓ at a void ratio of 0.46 (Foree and Reid, 1973), 450 mg/ℓ at a void ratio of 0.85 (Mueller and Mancini, 1975), and 1200 mg/ℓ at a void ratio of 0.68 (Plummer *et al.*, 1968). The average suspended solids concentration of 190 mg/ℓ at a void ratio of 0.94 as observed in this study compares favorably with other data and is probably due to the detention times which were higher than most other studies.

Effect of pH on Gas Production

After termination of the Phase I, II and III studies, all the analytical data were correlated with each other. When the daily gas production rates were related to the effluent pH values, the results in Figure 15 indicate that the highest rates are observed at a pH of 7.1. The relatively low gas production rates at a pH of less than 6.9 were observed during the period of heavy metal toxicity. The rate of optimum pH values as observed in the present study is considerably smaller than other researchers have found (Figure 16). Speece and Clark (1969), for example, still obtained half of the optimum gas production rates at a pH value of as low as 5.4, using anaerobic filters fed with acetate. However, they related gas production to the average pH at different depths in the plug-flow unit and a more narrow band would have been obtained if the pH in the effluent had been used for such comparison.

Clark and Speece (1970) also summarized existing literature data relating gas production of anaerobic digesters to corresponding pH values, indicating that at a pH of 6.0 the gas production was reduced by 50 percent. Using laboratory digesters, Thiel *et al.* (1968) came to a similar conclusion. Heukelekian and Heinemann (1939) measured the viable anaerobic bacteria at different pH values and noted a more gradual decrease at decreasing pH values as compared with the other studies. Speece and Clark (1969) noted that the inhibition of the methane fermenting bacteria at low pH values was bacteriostatic rather than bactericidal and could be reversed after pH adjustment. The inhibition at low pH values was attributed to hydrogen ions and undissociated fatty acids, while the lower gas production at high pH was thought to be due to unionized ammonia. It also could result from substrate limitation as at high pH all the fatty acids are dissociated and therefore not available for substrate uptake. McCarty and McKinney (1961) reported that free ammonia becomes toxic at concentrations of 150 mg/ℓ. Since the high pH values in the present study generally occurred at low loadings, the low gas production at higher pH values is likely due to substrate limitation. The average NH_3-N concentration in the effluent was 540 mg/ℓ which value did not change considerably during the study period.

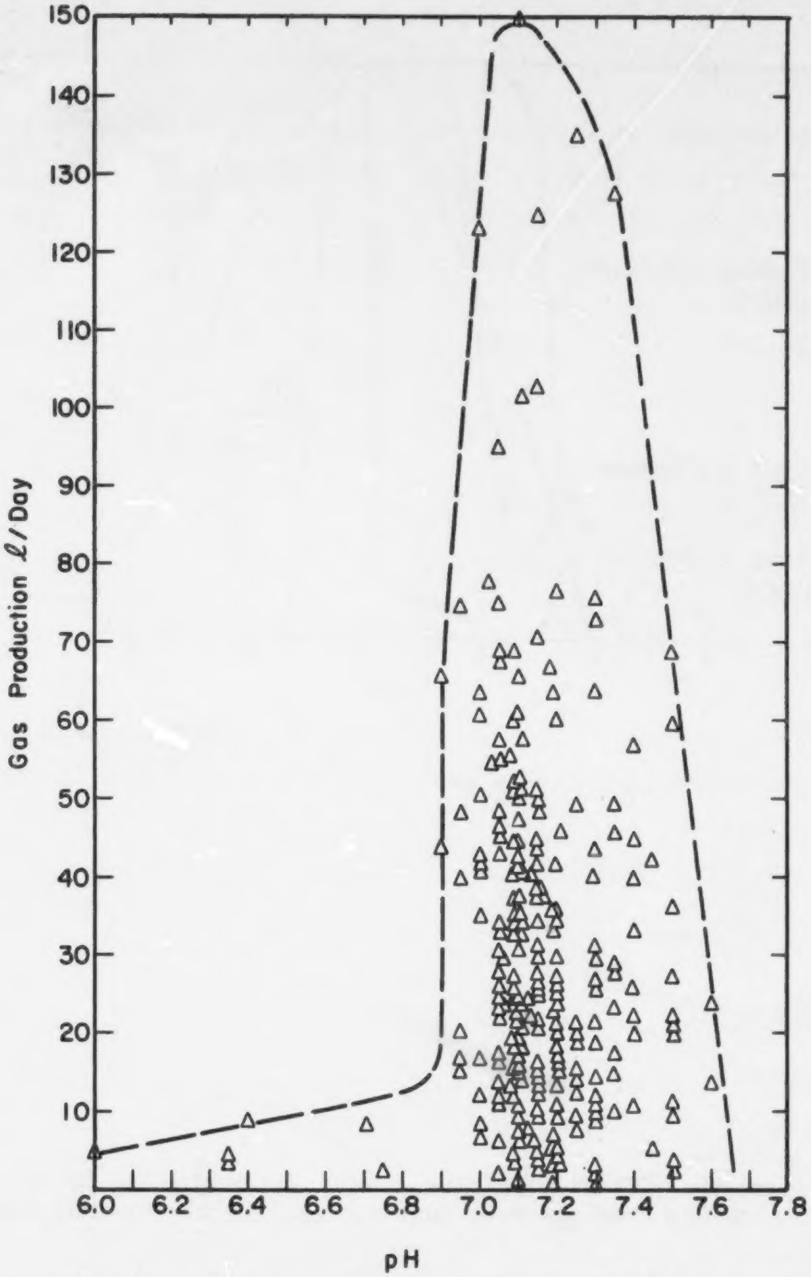

Figure 15. Effect of Effluent pH on Corresponding Rate of Gas Production

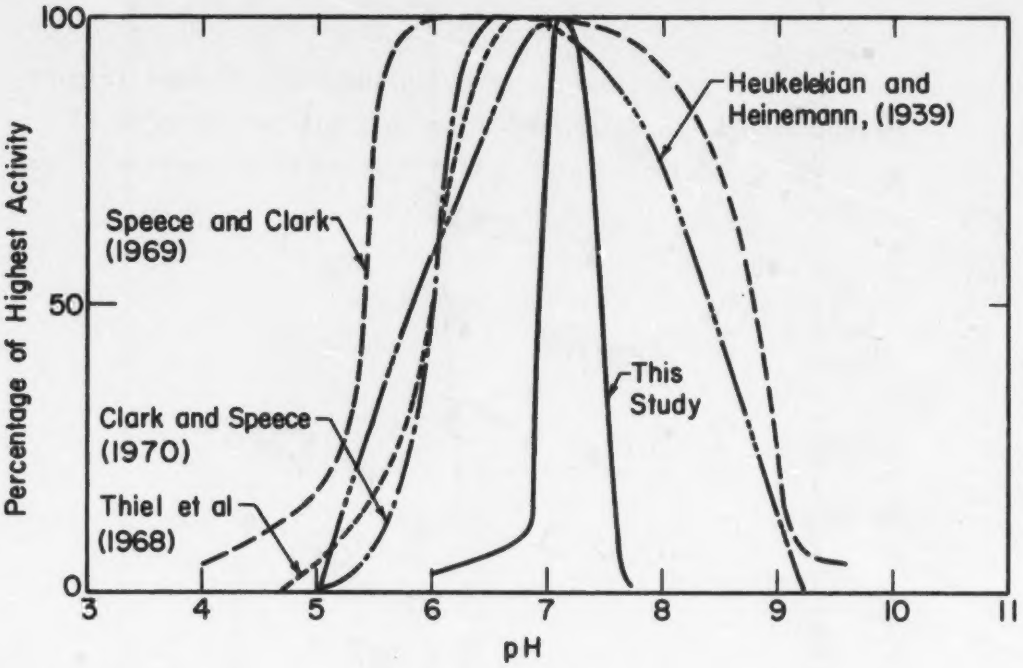

Figure 16. Effect of Effluent pH on Corresponding Relative Rate of Gas Production as Observed by Several Investigators

This would only correspond to about 10 mg/ℓ free ammonia at the pH of the effluent which is well below the stated toxic level.

Gas Composition

The gas composition measured in the present study was within the range of values reported by other investigators studying anaerobic filters (Figure 17). The methane content was generally 75 percent but decreased to 63 percent at the highest loading. Using a similar type of wastewater, Foree and Reid (1973) reported a 70 percent methane content. The decrease of the methane content at higher rates of substrate removal was also observed by Thiel *et al.* (1968) who noted that such a decrease corresponded to an increase in free volatile fatty acids and a decrease in pH. This also resulted in a higher CO_2 liberation and a lower bicarbonate alkalinity in solution. Speece and Clark (1969) similarly noted a 95 percent methane content at a pH of 8 which linearly decreased to 70 percent at pH 7, 50 percent at pH 6 and 30 percent at pH 5.

The amount of gas produced in the present study always corresponded closely to the amount of organic matter removed. During the three increasing loadings (Figure 10 and 11) the amount of methane gas corresponded respectively to 95 percent, 93 percent and 92 percent of the amount of COD removed. This is in close agreement with results obtained by Foree and Reid (1973) who recovered 99 percent using a similar waste stream. Using a fatty acid waste stream Young and McCarty (1968, 1969) recovered 100 percent, while Speece and Clark (1969) obtained 94 percent. A waste stream containing carbohydrates resulted in a recovery of 93 percent (Young and McCarty, 1968, 1969) 100 percent (Mueller and Mancini, 1975), more than 100 percent (Foree and Lovan, 1971). Jennett and Dennis (1975) on the other hand only accounted for 50 percent of the theoretical gas production at low loadings which, however, increased to 90 percent at higher loadings. El-Shafie and Bloodgood (1973) similarly only accounted 50 percent of theoretical gas production, while Caudill (1968) only observed 10 percent of the theoretical production. It was noted in the present study that the wet gasmeters did not register satisfactory at relatively low gas flow rates which may explain the results obtained by Jennett and Dennis (1975).

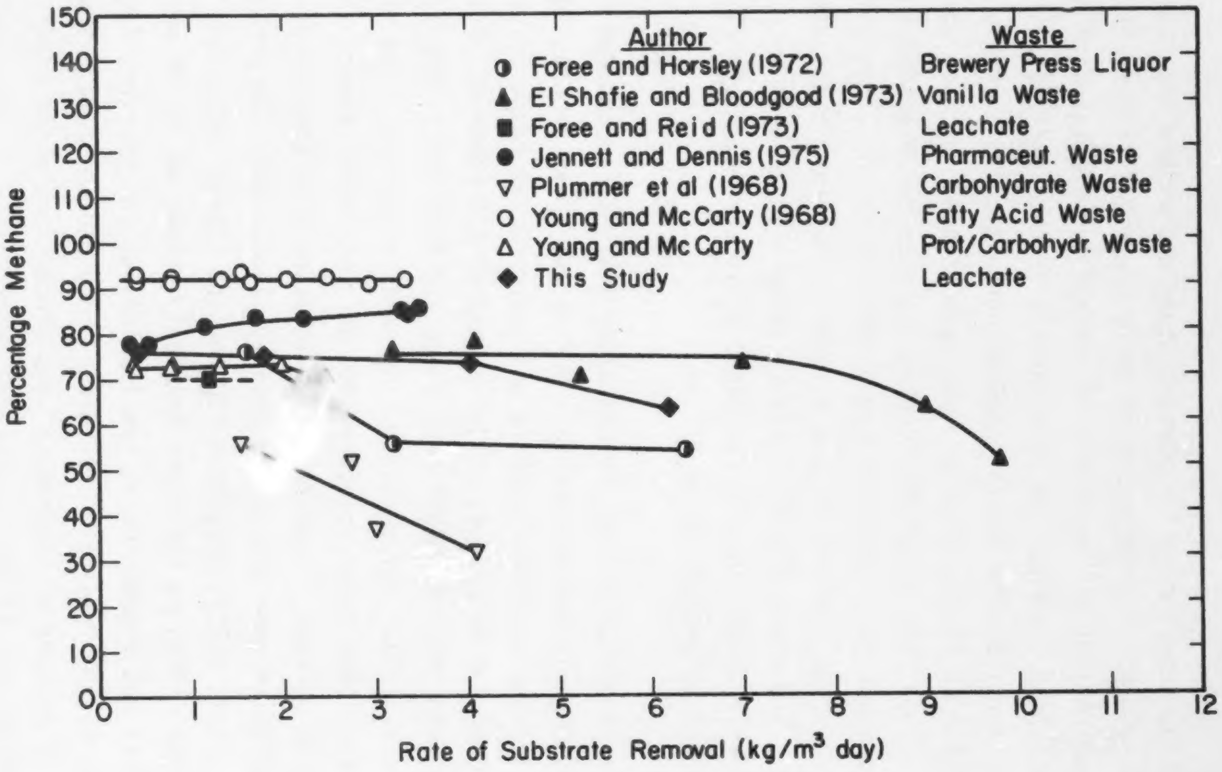

Figure 17. Effect of Rate of Substrate Removal on Gas Composition

Effluent Buffer Capacity

It was noted in the previous section that several factors influenced the pH and buffer capacity of the system. Figure 10 and 11 indicated that the alkalinity as determined by titration was relatively insensitive to changes in the bicarbonate concentration as measured with the inorganic carbon channel of the TOC analyzer. This is a result of the ionized fatty acids which register in the alkalinity determination, but are not very effective in maintaining the pH of the solution due to their low pK values. It was therefore not surprising to note a general decrease in the inflection point of the effluent titration curve and the fatty acid concentration in the effluent (Figure 18). This then shows that the alkalinity as deetermined by titration is not a useful monitoring tool to measure the buffer capacity of the system, and more useful information is obtained when both the pH, inorganic carbon and fatty acid concentrations are monitored.

Kinetics of Substrate Removal

The kinetic consideration discussed earlier indicate that at relatively low substrate concentrations the removal rate increases linearly with effluent concentration. A compilation of the different studies evaluating anaerobic filters indicate that this is indeed the case (Figure 19). The rate of substrate removal was calculated as kilograms of COD removed per m^3 empty column volume per day; while the effluent concentration was used as the corresponding substrate concentration.

Considerable spread in the results of the different studies is apparent (Figure 19), indicating that other factors such as specific surface area, biodegradability, temperatures and mixing regime also exert a significant influence. Figure 19 also indicates that several effluent concentrations have a finite value when the removal rate approaches zero. The highest such residual concentration was noted in the present study and extrapolation would indicate a valuesof about 850 mg/ℓ. Four other studies showed such residual concentration. Further evaluation indicated that its magnitude generally increased with increasing influent concentrations. Residual effluent and related influent concentrations reported by these studies

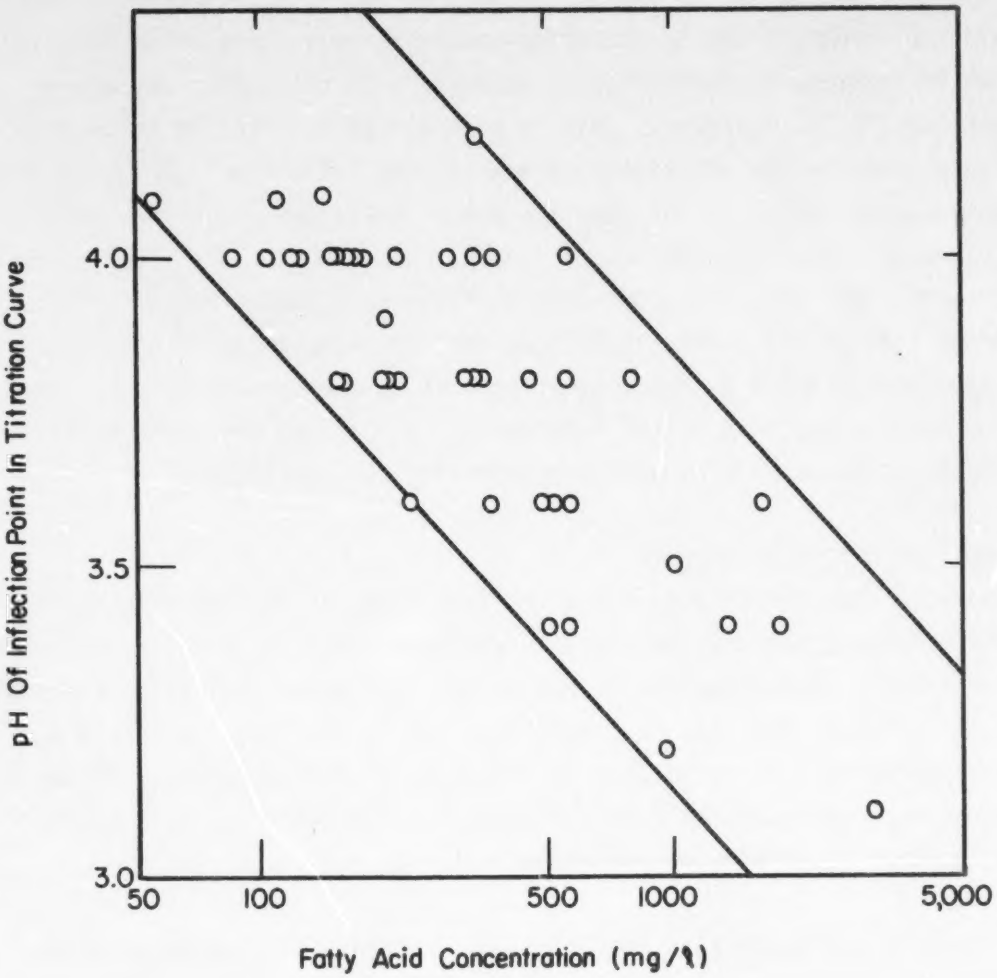

Figure 18. Relation Between pH of Inflection Point and Fatty Acid Concentration

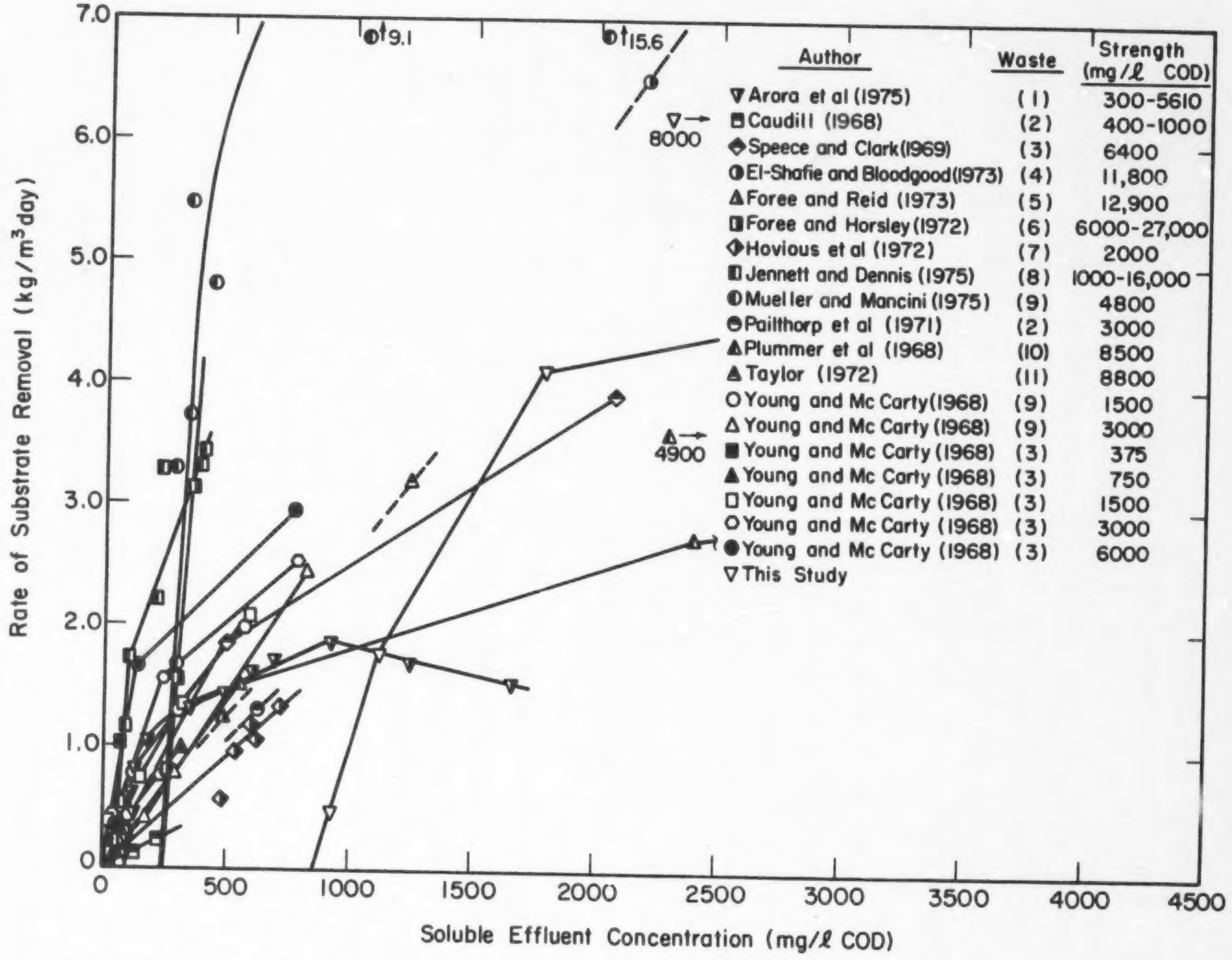

Figure 19. Effect of Substrate Removal Rate on Effluent Concentration as Measured in Different Studies using Various Wastes

were 850 mg/ℓ and 32,000 mg/ℓ (present study), 240 mg/ℓ and 13,000 mg/ℓ (Foree and Horsley, 1972), 230 mg/ℓ and 4,800 mg/ℓ (Mueller and Mancini, 1973), 100 mg/ℓ and 500 mg/ℓ (Arora *et al.*, 1975) and 50 mg/ℓ and 1,000 mg/ℓ, respectively (Jennett and Dennis, 1975). As higher influent concentrations correspond with a higher biomass present in the unit, the higher residual organics could also be the result of bacterially released organics or organics liberated during cell lysis. As a result of the presence of such residual concentrations, the slope of the relation between dF/V·dt and S_b (Equation 11) reached an almost infinite value; the k_2 (in Equation 11) values could therefore not be used for further analysis.

The data in Figure 19 also show that the substrate removal rates in only three studies approached a limiting value at high substrate concentrations. The result of one of these studies even showed a decreasing removal rate at such high concentrations indicating substrate inhibition (Arora *et al.*, 1975). According to Equation (8), a square root relationship would be obtained between the rate of substrate removal and substrate concentration at high concentrations. The data in the present study resulted in an exponent of 0.3 while the data of Plummer *et al.* (1968) gave a value of 0.4 which is less than the predicted value of 0.5. At veyr high concentration, dF/V·dt is expected to become independent of S_b as a result of which the value of the exponent decreases below 0.5 as observed in these two studies. This would indicate the validity of the model; however, insufficient data are as yet available to make a final conclusion.

A disadvantage of the model described by Equation (8) is that it does not define a maximum rate of substrate removal at high substrate concentrations. Such value, however, can be obtained by assuming that dF/V·dt and S_b follows a Monod hyperbolic relationship, whereafter the constants can be determined for a Lineweaver-Burk plot. When the reciprocal substrate removal is plotted versus that of the substrate concentration, a satisfactory linear relationship was not obtained. However, by using only the lowest values a maximum substrate removal rate of 7 kg COD/m^3 day and a half saturation concentration K_s of 1,500 mg/ℓ were calculated. The results of Plummer *et al.* (1968) gave values of 3.5 kg COD/m^3 day and 850 mg/ℓ respectively using three of the four reported data points. These maximum rates also tended to increase with biodegradability of the substrate and were 1.8 kg COD/m^3 day with a corresponding BOD/COD ratio of 0.52 (Arora *et al.*, 1975), 3.5 kg COD/m^3 day with a BOD/COD ratio of 0.61 (Plummer *et al.*, 1968) and 7 kg COD/m^3 day with a BOD/COD ratio of 0.65 (El-Shafie and Bloodgood, 1973). Of all studies, the highest rate was reported by Mueller and Manzini (1975) who observed a removal rate of 15.6 kg COD/m^3 day using a biodegradable dextrose-peptone mixture.

Specific Surface Area

Both Equation (8) and (11) indicate that the specific surface is the next most important factor determining the rate of substrate removal. When the $k_2 \cdot \frac{A}{V}$ values (in Equation 11) obtained by dividing the rate of substrate removal by the substrate concentration obtained at low substrate concentrations were related to the specific surface area in each reactor, no definitive correlation was observed (Figure 20). Excluded from Figure 20 were the data from those studies in which an increase in removal rate did not correspond to an increased substrate concentration as a result of which the k_2 values approached infinity. This was mainly due to the fact that none of the studies evaluated specific surface areas using the same substrate. Five studies, that evaluated the effect of specific surface areas using aerobic trickling filter, are included in Figure 20 and all show an increasing k_2 value as a result of the increasing surface area as predicted by Equation (11). The relation tends to be linear at low surface areas but becomes less than linear at high surface areas. This can be attributed to the bacterial growth which tends to fill up the void spaces as result of which the specific surface area at the liquid-biofilm interface becomes smaller than the specific surface area of the filter medium. Thus, although insufficient data are available from the different anaerobic filter studies, all results shown in Figure 20 tend to indicate that the value of k_2 would increase with increasing surface area. As synthetic media having large surface areas are several times more expensive than the rock media generally used, selection of the required specific surface area should be based on economic considerations.

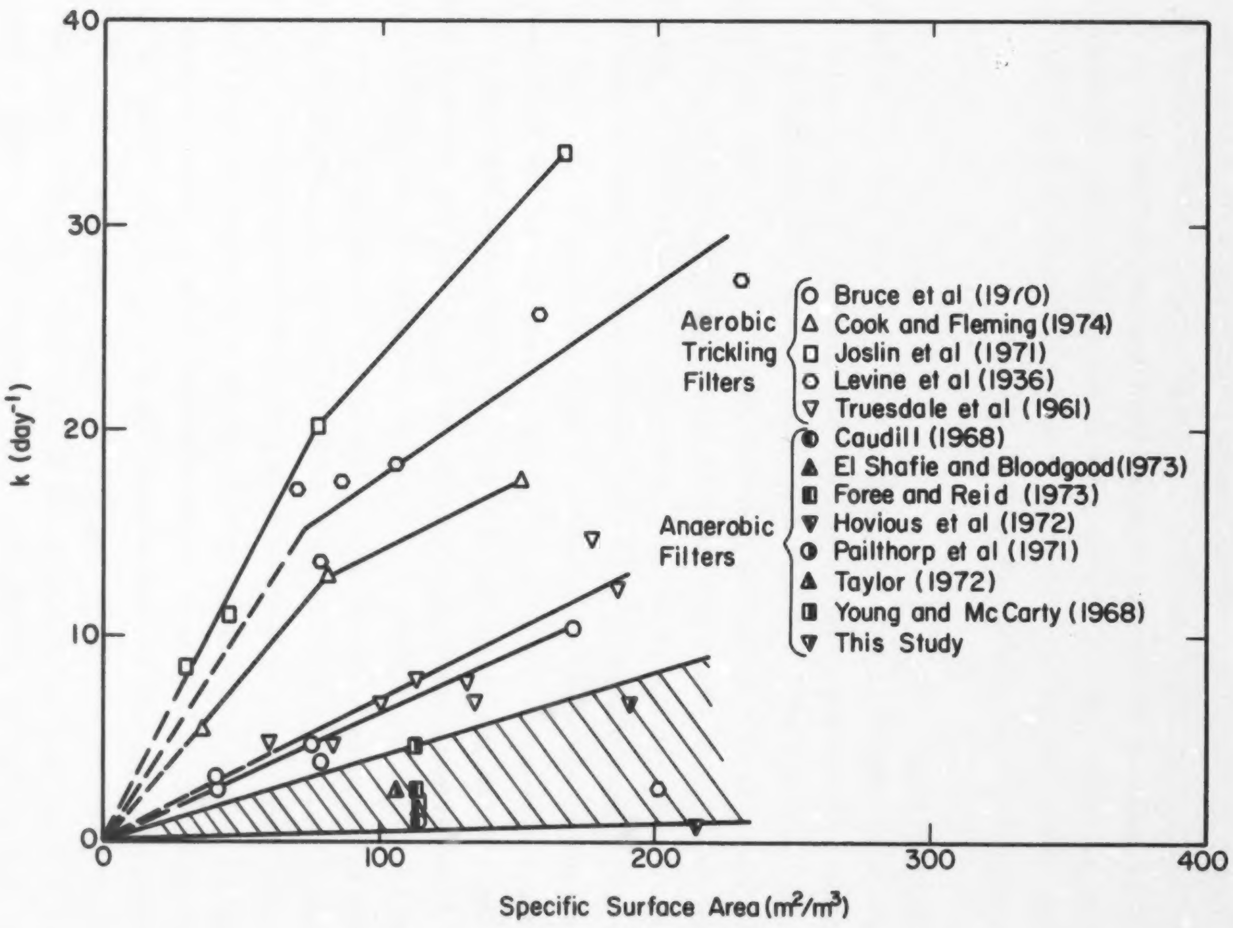

Figure 20. Effect of Specific Surface Area on Substrate Removal Coefficient

Temperature

The effect of temperature on rate of substrate removal was evaluated in only two studies. Tadman (1973) using an industrial waste and column filled with Intalox saddles observed a 10 percent increase in removal efficiency when the temperature was increased from 25°C to 35°C. Caudill (1968) noted a 27 percent improvement in effluent quality when the temperature of an anaerobic filter unit treating a dilute fatty acid solution was increased from 26°C to 37°C. A preliminary comparison of heating costs versus the cost associated with increasing the specific area in the column by installing more expensive high surface area synthetic filter medium would indicate that the latter alternative is less costly in order to reach a desired treatment efficiency.

Mass Transfer

The effect of the flow velocity on the mass transfer in anaerobic filters as illustrated in Equations (11) (12) and (13) is difficult to evaluate. The most accurate data to illustrate this effect were obtained from the study by Young and McCarty (1968, 1969) when for a given flow rate in the column the substrate removal rate in each 30 cm segment was calculated and related to the concentration leaving that segment. Such calculations resulted to the concentration leaving that segment. Such calculations resulted in relations similar to those shown in Figure 19. The calculathe $k_2 \frac{A}{V}$ values showed a linear increase with actual flow rates within the column when plotted on log-log paper. From the limited data an exponent of 0.46 was calculated at flow velocities ranging from 1 to 10 m/d, which approaches the value of 0.5 predicted by Takeshi *et al.* (1972). Since the value of k_2 is related to K_L, this in turn indicates that it is beneficial for a given column volume to minimize the diameter whil maximizing the height of the column in order to obtain higher velocities and thus higher Reynolds numbers within the column.

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II

PHYSICAL CHEMICAL TREATMENT OF LEACHATE AND ANAEROBIC FILTER EFFLUENT

CONCLUSIONS

It was concluded that high-strength leachates cannot be effectively treated by physical-chemical treatment methods such as activated carbon adsorption, chemical precipitation and chemical oxidation. Activated carbon was observed to have a relatively low sorptive capacity when used to treat high-strength leachates. Although free volatile fatty acids, major constituents of such leachates, have a relatively low sorptive capacity, even lower capacities were noted for the non-fatty-acid fraction in leachate using activated carbon adsorption isotherms. Although an initial removal rate as high as 72% was obtained in activated carbon columns through which the diluted leachate was passed, much lower removal percentages were observed after passage of several bed volumes, and almost complete breakthrough occurred after 200 bed volumes. The column studies also illustrated the lower removal rate for the non-fatty-acid fraction in leachate. Activated carbon treatment of leachate is also unfeasible because headloss builds up rapidly in the column with the formation of iron precipitates. Although most of these precipitates were removed in the first backwash, difficulty was again encountered in subsequent runs.

Substantially higher adsorptive capacities of activated carbon were found for biologically pretreated leachate. Removal of biodegradable organics with an anaerobic filter increased the adsorptive capacity by 50%. Aerated lagoon treatment of the anaerobic filter effluent further removed low-molecular-weight organics, resulting in an adsorption capacity of 0.174 mg TOC/mg AC, a value approximately 2.5 times that observed for untreated leachate. Batch sorption tests showed that color and aromatic hydroxyls are removed at lower carbon dosages than are high-molecular-weight carbohydrate-like materials. Membrane fractionation of the anaerobic filter effluent followed by activated carbon column treatment of each fraction showed relatively low removal rates for both the high-molecular-weight organics collected in the 18,000 MW UF retentate and the low-molecular-weight organics present in the 150 MW RO permeate. The highest removal rates were observed for fulvic-like organics of intermediate molecular weight. The increase in removal rates of organics in anaerobic filter effluent treated by aerated lagoon as mentioned previously was attributed to the higher adsorption characteristic of the low-molecular-weight organics.

Organic matter removal by lime precipitation, both before and after aeration, produced removal rates as low as 20 to 25%, and this removal was obtained at excessively large dosages. Other physical-chemical methods tested, such as ozonation and chlorination, resulted in similarly low organic matter removal rates. These results clearly show that physical-chemical treatment methods are not feasible for high-strength leachates and that extensive biological pretreatment is required. Of all physical-chemical methods tested, activated carbon treatment produced the highest organic matter removal rates.

INTRODUCTION

Solid waste leachate generated as a result of infiltrating rainwater contains high concentrations of organic matter. These substances can be removed by physical-chemical or biological treatment processes. After analyzing leachate samples from landfills of different ages, Chian and DeWalle (1975) noted a change in organic matter composition with increasing age of the fill: the percentage of free volatile fatty acids decreased, while the amount of refractory fulvic-like organics increased with age. Since free volatile fatty acids, di- and tricarboxylic acids and alcohols are degradable by aerobic and anaerobic bacteria, it was recommended that aerated lagoons and anaerobic filters be employed to remove organics from landfills which have generated leachate only recently. Physical-chemical methods such as lime coagulation, activated carbon adsorption and ozonation are generally less effective in removing such organics. Refractory organics generally formed by bacterial or chemical processes after removal of the degradable substrate, on the other hand, are more amenable to removal by physical-chemical processes then by bacterial processes.

The above recommendations have been borne out by several studies on the treatability of leachate. While Boyle and Ham (1974) noted a 93% COD removal in anaerobic digestors, Ho et al. (1974), using a similar leachate, obtained only a 34% COD removal rate using activated carbon at a maximum dosage of 20,000 mg/l. In subsequent column studies with granular Filtrasorb 400, maximum COD removal rates of up to 59% were observed at detention times greater than 20 minutes, based on analysis of the filtered second bed volume of leachate passed through the column. A pH reduction of the leachate to reduce the ionization of the dissociated free volatile fatty acids and to enhance their adsorption did not result in increased COD removal; in fact,the opposite was observed, with high COD removals corresponding to high pH. A similar comparison showed that anaerobic digestors were able to remove 99% of the leachate COD, while activated carbon at a dosage of 160,000 mg/l removed only 60%. The leachate studied was generated from a relatively recent fill, and 65% of the 2000 mg/l of TOC consisted of free volatile fatty acids. The study further noted that the non-fatty-acid fraction of the organic matter was adsorbed preferentially to the fatty-acid fraction. After biological treatment of a similar leachate, Pohland and Kang (1975) obtained removal rates as high as 91%, indicating that biological treatment followed by carbon adsorption will result in high organic matter removal rates. Cook and Foree (1974) obtained 68% COD removal in the first effluent bed volume when leachate was passed through an activated carbon column. Lime coagulation prior to the activated carbon treatment increased the overall COD removal to 81%. Van Flect et al. (1974) observed a 71% COD removal in the first effluent bed volume when leachate was passed through an activated carbon column. Aluminum pretreatment resulted in an overall COD removal rate of 94%. The highest COD removal percentage, 85%, was observed by Roy Weston Inc. (1974) at a carbon dosage of 10,000 mg/l. Because the leachate was obtained from an old abandoned fill which had undergone considerable biological stabilization, high adsorptive removals were to be expected.

These previous studies show that variable organic matter removal rates can be obtained in landfill leachate using activated carbon, a fact which may well reflect the variable nature of the organics. While activated carbon treatment of concentrated leachate from recently generating fills was not very effective, higher removal rates were obtained with leachate from more stabilized fills. High removal rates can perhaps be obtained with a combination of coagulation and adsorption or of biological pretreatment and adsorption. Chemical precipitation or chemical oxidation alone were not found to be very effective (Chian and DeWalle, 1976).

The purpose of the present study was to evaluate in greater detail the effect of organic matter composition on adsorptive behavior using leachate samples from different landfills, employing both adsorption isotherm tests and column studies. The effect of biological pretreatment using an anaerobic filter, with or without further aerobic effluent stablization, on activated carbon adsorption was studies more extensively, since preliminary work showed that this treatment sequence resulted in low organic matter concentrations.

MATERIALS AND METHODS

Batch adsorption tests were conducted with both undiluted and diluted leachate samples to which increasing dosages of activated carbon were added. The tests were conducted with Filtrasorb 400 (Calgon, Pittsburgh, PA) added to rectangular 250 ml precipitation bottles filled with 100 ml of the sample. Prior to adsorption, the leachate samples were filtered through a 0.45 µm Millipore membrane filter (Millipore, Bedford, MA) to remove the small amount of suspended solids initially present, since only the adsorption of soluble organics was to be evaluated in this study. After the carbon was added, the samples were shaken for 24 hours at 180 rpm. Distilled deionized water blanks to which activated carbon was added were included to correct for the small amount of organic compounds that dissolve from the carbon. The column studies were conducted with columns 15 cm and 30 cm long having empty bed detention times of 1.5 and 3.0 minutes, respectively, at a flowrate of 10 cm/min (2.5 gpm/ft^2) maintained by means of an accurate FMI positive displacement metering pump (FMI, Oyster Bay, NY). The columns were backwashed at a rate of 24 cm/min (6.0 gpm/ft^2) when the headloss buildup exceeded 200 cm. The leachate used for the carbon tests was obtained from a lysimeter filled with milled solid waste to which simulated rainfall was added (Chian and DeWalle, 1976).

Anaerobic biological pretreatment of the leachate was accomplished with the unit described in Chapter I. Further aerobic degradation was conducted in a 80-liter batch reactor. Before and after aeration the soluble organic matter was characterized by molecular weight and major classes of organics using colorimetric tests. The molecular weight distribution was estimated using Sephadex G-25 and G-75 columns (Pharmacia, Piscataway, NJ). Larger quantities of the various molecular-weight fractions were obtained with a preparative ultrafiltration unit HFA-180 (Abcor, Cambridge, MA) followed by concentration of the UF permeate with a reverse-osmosis B-10 Permeator (DuPont, Wilmington, DE).

Each fraction was passed through an activated carbon column. Batch coagulation studies were conducted using a 1-liter sample to which a lime slurry was added. Following addition of the slurry, the content was rapidly mixed at 100 rpm for 1 minutes followed by slow mixing for 20 minutes at 25 rpm. The liquid was then settled for 30 minutes. The various parameters were measured in the decanted supernatant.

RESULTS AND DISCUSSION

Initially, the adsorption of the organic matter in the concentrated leachate was evaluated. The results of these tests (Figure 21) show a relative low adsorptive capacity: 0.045 mg TOC/mg AC, corresponding to a maximum COD removal rate of 73% at the highest dosage. When the leachate obtained from the same lysimeter two years later was tested, its concentration had decreased to 29% of the initial concentration. Its adsorptive capacity, however, was 6.5 times as high, possibly indicating that gradual biological stabilization of the solid waste and of the interstitial leachate resulted in organics more amenable to physical adsorption. This explanation is also indicated by the results in Figure 21 since a higher maximum adsorptive capacity tends to be associated with a lower initial organic matter concentration. The positive effect of biological stabilization is further examplified by the results of Karr (1972), who noted a maximum adsorptive capacity of 0.16 mg TOC/mg AC using leachate without any biological treatment. Using a similar wastestream after aerobic biological treatment, Pohland and Kay (1975) obtained a capacity of 0.36 mg TOC/mg AC a factor of 2.3 higher. Since the free volatile fatty acids are dissociated at the pH of the leachate, higher adsorptive capacities are to be expected at decreasing pH values when these acids are no longer ionized. The results in Figure 21 indeed show the highest capacity at a pH of 4. The lowest adsorptive capacity was observed at a pH of 8. These results are contrary to those of Ho et al. (1974), who did not note any pH effect, quite possibly because of the absence of any fatty acids in the analyzed sample.

Since higher adsorptive capacities tended to be associated with lower initial concentrations, several adsorption tests were made at the lowest initial concentration noted in Figure 21; i.e., 120 mg/l TOC. Using the diluted leachate dated 6/12/73, a maximum adsorptive capacity of 0.068 mg TOC/mg AC was obtained (Figure 22), 1.48 times higher than the capacity

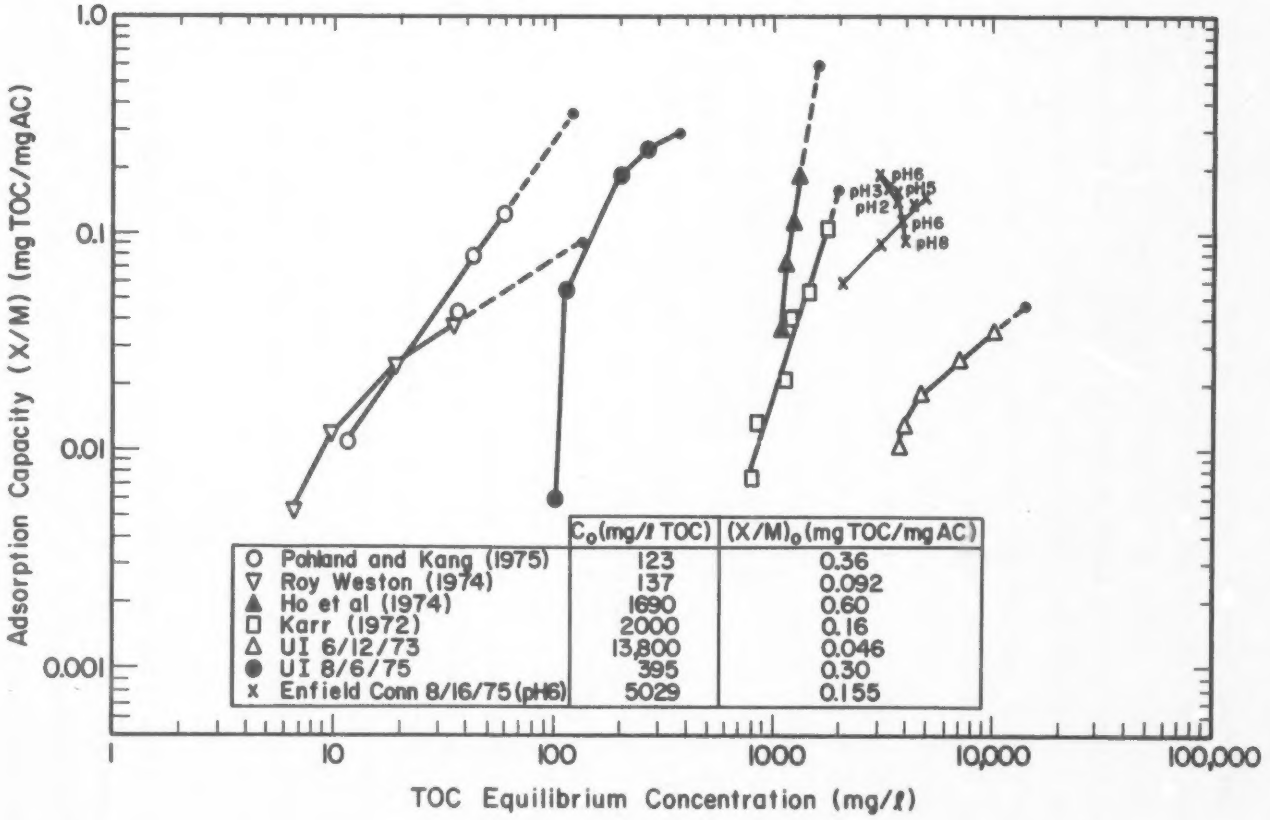

Figure 21. Activated Carbon Adsorption Isotherms with Different Leachate Samples

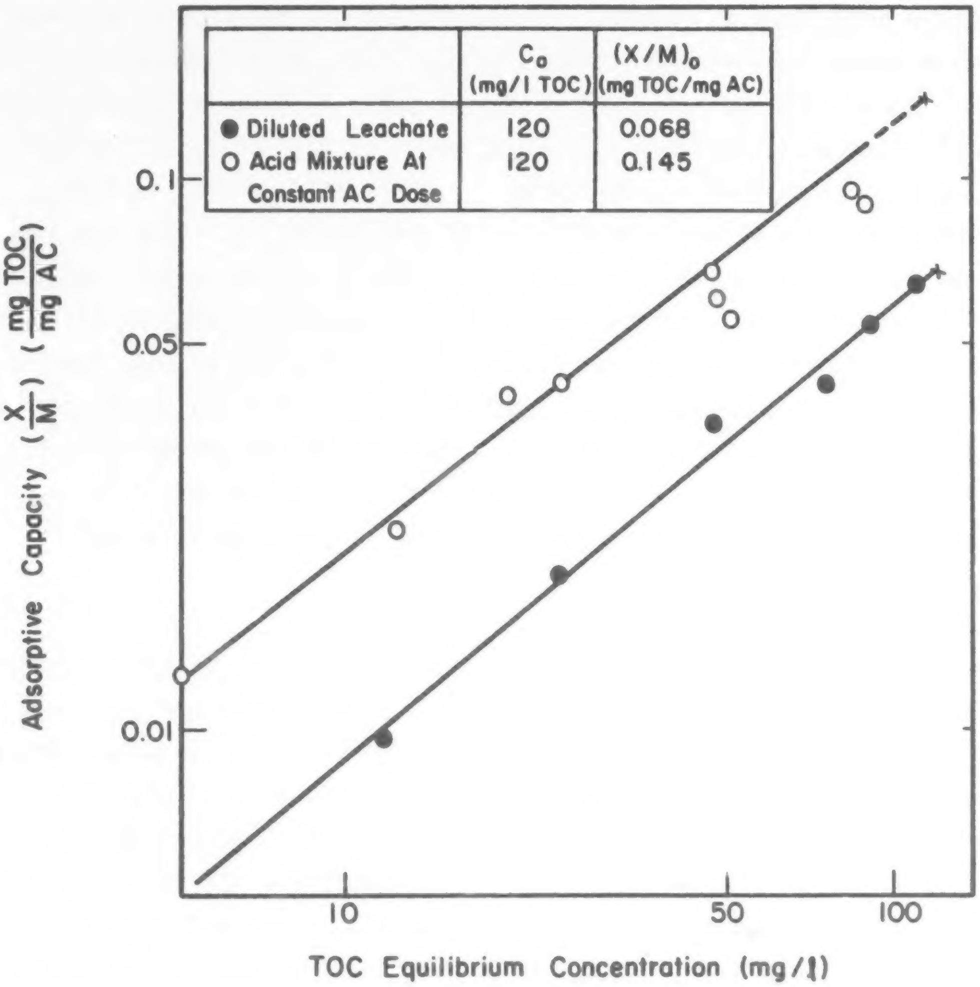

Figure 22. Activated Carbon Adsorption Isotherms with a Diluted Leachate Sample and a Fatty Acid Mixture

of the undiluted leachate, indicating that lower concentrations do correspond to higher capacities. The increase, however, is not as substantial as the increase of 6.5 times found for the biologically stabilized leachate. Since the free volatile acids comprised 52% of the organic matter in this leachate sample, an acid mixture was made having the same relative composition as the leachate sample; i.e., 20 mg/l formic, 50 mg/l acetic, 10 mg/l propionic, 50 mg/l butyric, 10 mg/l isobutyric, 10 mg/l paleric, 10 mg/l isovaleric, 70 mg/l hexanoic acid and 100 mg/l NaCl to give an initial TOC of 120 mg/l. Using this acid mixture, a maximum adsorptive capacity of 0.145 mg/l was observed 2.1 times as high as that obtained with the diluted leachate sample. This result indicates that the non-fatty-acid portion has a lower adsorption capacity than the fatty-acid fraction and that simple removal of the free volatile fatty acids, which occurs during aerobic biological stabilization, will not result in higher adsorptive capacities. Removal of the non-fatty-acid fraction and bacterial excretion or formation of refractory fulvic and humic acids may therefore be necessary before higher capacities are obtained.

Different methods of arriving at adsorption isotherms were next evaluated. While the results shown in Figure 22 for the acid mixture were obtained with a constant carbon dosage and increasing dilution of the acid mixture, the acid mixture results in Figure 23 were obtained with a constant organic matter concentration and increasing activated carbon dosages. Although the maximum adsorptive capacity in both cases was the same, the slope of the isotherm was lower using the constant carbon dosage; i.e., the value of n decreased from 1.0 to 0.79. Since the low adsorptive capacity at low equilibrium concentrations often results from the presence of a nonadsorbable fraction, dilution of the organic matter concentration and therefore reduction of the nonadsorbable fraction at a constant carbon dosage will result in a higher adsorptive capacity than will the use of an undiluted sample with increasing carbon dosages, since even very high carbon dosages will not remove this nonadsorbable fraction.

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16. ABSTRACT

A completely mixed anaerobic filter was found to effectively remove organic matter concentrations in high-strength solid waste leachate over a range of organic loadings and shockloads. Recirculation eliminated the need for buffer solutions. Testing of a fixed film biological reactor model showed that the substrate removal rate is primarily affected by substrate concentration, specific surface area, flow rate, and temperature of the unit. Studies of the biological aerated lagoon or extended aeration process were conducted in six completely mixed reactors (no recycle) fed with undiluted leachate. Phosphate requirements of the aerobic biomass were extensively evaluated. Kinetic constants were calculated for optimum conditions. The settling and dewatering characteristics of the sludge from the aerated lagoons were studied. The combined treatment of leachate and municipal sewage in a conventional plugflow activated sludge unit was found to effectively treat high strength leachate. The test unit was not able to treat the high strength leachate at $\geq 4\%$ of the municipal sewage flow rate. Physical-chemical treatment methods are not effective in removing large quantities of organics from the leachate and that biological pretreatment is required; these methods were therefore tested using aerated lagoon effluents. Ozonation, activated carbon, anion exchange resins, and reverse osmosis were studied. Treatment costs were estimated for leachate flows of 7.6 and 76 ℓ/min containing 5000 and 25,000 mg/ℓ BOD_5.

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Volume II

Biological and Physical-Chemical Processes

by

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

This study involved extensive analysis of different organics and inorganics present in leachate samples from landfills located in different regions of the United States. These analysis were then used to predict the effectiveness of different biological and physical chemical treatment methods for contaminant removal.

Francis T. Mayo, Director
Municipal Environmental
Research Laboratory

ABSTRACT

The efficiencies of three different types of biological treatment units in removing organic matter from solid waste leachate were extensively evaluated. The units studied were the anaerobic filter, the aerated lagoon, and an activated sludge unit treating combined leachate and municipal sewage. The effectiveness of physical-chemical treatment steps in further removing organic matter from the biological unit effluents was also examined.

A completely mixed anaerobic filter, in which the influent is diluted with recirculated effluent, was studied for a 52-day period and found to effectively remove organic matter concentrations in high-strength, solid waste leachate over a range of organic loadings and shockloads. Recirculation increases the acidic pH of the feed, eliminating the need to add the costly buffer solutions required in plugflow anaerobic filters. Ninety-nine percent of the COD removed in the unit was accounted for in the methane produced. This valuable energy source can be used for combustion to heat the unit. A microbial solids balance indicated that only 0.012 grams of VSS was produced per gram of COD removed. Because of the low solids production and initial seeding of the unit with digested sludges, it was not necessary to add nutrients. Although a possible heavy metal toxicity was observed, it was eliminated by adding sulfide. A high organic matter removal percentage was observed at hydraulic detention times greater than 7 days, but the percentage was considerably lower at shorter detention times. Increases in organic loading had a substantial effect on the relative organic matter composition of the effluent. Testing of a fixed film biological reactor model showed that the substrate removal rate is primarily affected by substrate concentration, specific surface area, flow rate, and temperature of the unit.

Evaluation of various physical-chemical treatment methods such as chemical precipitation, activated carbon adsorption, and chemical oxidation showed that these methods were not very effective in removing organic matter from high strength leachate. Although free volatile

fatty acids, present in large quantities in leachate, have a relatively low activated carbon adsorption capacity, even lower capacities were noted for the non-fatty acid fraction using batch isotherms. Although relatively high organic matter removals were obtained using activated carbon columns, rapid breakthrough occurred after passage of the initial bed volume of effluent. Activated carbon treatment of the high strengh leachate was found to be unfeasible because of rapid headloss buildup resulting from the formation of iron precipitates in the carbon column. These solids are difficult to remove in subsequent backwash operations. The organic matter removal rate achieved using lime precipitation was as low as 26% and was realized only at very high dosages.

Substantially higher adsorptive capacities were observed for biologically pretreated leachate. Removal of biodegradable organics with an anaerobic filter increased the adsorption capacity by 50%, while aerated lagoon treatment of the anaerobic filter effluent resulted in an adsorptive capacity 2.5 times higher than that of untreated leachate. Membrane fractionation of the anaerobic filter effluent followed by activated carbon column treatment of each fraction produced relatively low removal rates for both the high-molecular-weight organics collected in the 18,000 MW UF retentate and the low-molecular-weight organics present in the 150 MW RO permeate. The highest removals were observed for the intermediate-molecular-weight fulvic-like organics which were also characterized by a high aromatic hydroxyl group content. Aerated lagoon treatment of the anaerobic filter effluent resulted in organic matter removals as high as 79% using activated carbon columns. This increased removal rate was shown to result from the higher adsorption characteristics of the low molecular weight organics present in the 150 MW RO permeate. Anaerobic filter treatment of the leachate resulted in lower organic matter removal rates than were obtained with untreated leachate. Aerated lagoon treatment of the anaerobic filter effluent resulted in a slightly higher TOC removal of efficiency. Both removal rates, however, were obtained only at very high lime dosages, precluding the use of this treatment method as a feasible alternative to activated carbon. It was therefore concluded that physical-chemical treatment methods are only effective after extensive biological pretreatment. Of all physical-chemical methods tested, activated carbon treatment was the most effective in removing organic matter.

Studies of the biological aerated lagoon or extended aeration process were conducted in six completely mixed reactors with no recycle fed with undiluted leachate and maintained at detention times of 85.7, 60, 30, 15, and 7 days. These units were operated for periods from 70 to 150 days. The resulting average TOC removal efficiencies varied between 99% and 96.8% at organic loadings ranging from 0.224 kg/m^3·day (14 lb TOC/1000 cu ft·day) to 1.65 kg/m^3·day (105 lbs TOC/1000 cu ft·day). The phosphate requirements of the aerobic biomass were extensively evaluated. The 30 day aerated lagoon did not show any deterioration when the COD:P ratio in the influent was increased from 165:1 to 300:1. A significant increase in effluent TOC values was observed, however, when the ratio was increased to 800:1. Such low ratios did not affect the 60 day and the 87.5 day units, which were able to function at a ratio as high as 1540:1; the sludge settling characteristics, however, deteriorated substantially at this ratio. Cessation of nutrient addition to the units having relatively low detention times caused an immediate increase in effluent organic matter concentrations and a decrease in MLVSS. Calculations using the effluent data and MLVSS values obtained under optimum conditions indicated that the bacteria yield was 0.42 mg VSS/mg COD, the respiration rate content was 0.025 day^{-1}, and the overall first-order substrate removal rate constant was $4.9 \cdot 10^{-4}$ liter/mg VSS·day. All units showed high heavy metal removal rates, especially for iron (99.9%), while low rates were observed for calcium (99.3%) and magnesium (75.9%). The lowest removal rates were obtained with sodium (24.1%) and potassium (17.0%).

The settling characteristics of the sludge from the aerated lagoons were found to be comparable to those of lime softening sludge and primary sludge, which have higher settling rates than observed for secondary sludge. The interface settling rates generally decreased during conditions of nutrient limitations. The dewatering characteristics of the sludge were greatly improved by adding cationic polymers and inorganic coagulants. An increase of approximately 20 times in specific resistance was obtained at a polymer dosage of 1.5% (Nalco 73C32) and 2.3% (Primafloc C_7) and at coagulant dosages of 14.8% ($FeCl_3 \cdot 6H_2O$) and 23.7% ($Ca[OH]_2$). These increases generally corresponded to increases of 6 times in vacuum filler yields. Analysis of the effluent of the 30 day aerated lagoon showed that 97.6% of the organics had molecular weights greater than 100, with 33% in the range from 100 to 500, 41% in the range from 500 to 5000, 20% in the range from 5000 to 50,000 and 4% greater than 50,000, indicating that these organics are amenable to reverse osmosis and activated carbon treatment but not to chemical precipitation.

It was also found that physical-chemical treatment methods are not effective in removing large quantities of organics from the leachate and that biological pretreatment is required. Several physical-chemical methods were therefore tested using the aerated lagoon effluents. While ozonation removed only 48% of the lagoon effluent TOC after a 3 hour treatment period, activated carbon columns were able to remove 86% of the organic matter using an empty bed detention time of 3.7 minutes. A maximum initial COD removal of 53% was realized with a weak base anion exchange resin, while 82% and 85% of the COD was removed using strong base anion exchange resins. Membrane reverse osmosis was the only process capable of removing 91 to 96% of the salts initially present at a TDS concentration of 6200 mg/l. The organic matter removal rates using reverse osmosis ranged from 86% to 97%. These rates were not enhanced by ion exchange or activated carbon pretreatment. Removal of suspended solids by sand filtration or chemical precipitation is likely required for reverse osmosis, activated carbon, or anion exchange resin treatment of the aerated lagoon effluent.

The combined treatment of leachate and municipal sludge was evaluated in a conventional plugflow activated sludge unit. It was found that the test unit could effectively treat the high strength leachate. Directly after the addition of leachate the effluent BOD and COD concentration deteriorated somewhat, but after sufficient adaptations the effluent qualities were generally comparable to that of the control units. While BOD values were not greatly affected, COD concentrations showed a gradual increase as more leachate was added. The test unit was not able to treat the high strength leachate at 4% of the municipal sewage flow rate, as evidenced by high effluent BOD values and deteriorating sludge conditions. This failure was attributed to limiting phosphate concentrations in the influent and the relative composition of the soluble high molecular weight organics which tend to affect the flocculation of the sludge.

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RECOMMENDATIONS FOR FURTHER RESEARCH

Biological methods of high-strength leachate treatment which were not evaluated because of budget constraints included the fixed media unit (trickling filter and rotating disk), the anaerobic lagoon, and modified soil treatment system currently being tested at the University of Illinois. It is therefore recommended that these systems be studied on a laboratory scale before being applied at the demonstration level.

Much research is needed to optimize the design and operation of anaerobic filters. The type of solid media to which the bacteria are attached should first be studied in a series of parallel tests using various soft materials and shapes. The substrate removal efficiency over a range of loadings should be evaluated and the amount of solids leaving the unit through the effluent should be determined. The second phase should evaluate different feed configurations, such as conventional plugflow feeding, step feeding, and tapered step feeding and the location of the recirculation outflow. Different filter shapes (heights and widths), all having the same volume, should be tested for a given volume, since a low but long unit is less expensive than a low but wide unit, and the amount of substrate removed is likely to be higher in the latter unit. The third phase of the study should focus on operational modes of the filter, and the effect of different recirculation flowrates and operating temperatures should be tested in parallel.

An extensive study should be conducted to determine when leachates are sufficiently biologically stabilized to be effectively treated by physical-chemical methods. The study should combine an in-depth organic chemical analysis of different leachate samples with a limited treatability study.

Finally, research should be undertaken to evaluate combined physical-chemical and biological methods, such as biological aerated lagoons to which powdered carbon is added or activated carbon upflow columns in which a biomass is maintained. The application of such treatment methods could enhance the life and flexibility of leachate treatment units already constructed and in operation.

I

TREATMENT OF A HIGH STRENGTH SOLID WASTE LEACHATE WITH A COMPLETELY MIXED ANAEROBIC FILTER

CONCLUSIONS

A completely mixed anaerobic filter, in which the influence organic matter concentration is diluted with recirculated effluent, was found to effectively remove organic matter concentrations in high strength municipal solid waste leachate at a range of organic loadings and shockloads. Recirculation can effectively increase the acidic pH of the feed to a pH value close to the optimum, thus eliminating the addition of costly buffer solutions as is required for the plugflow anaerobic filter. In the anaerobic filter, complex organics in the feed are hydrolyzed, first by acid fermenting bacteria to free volatile fatty acids, primarily acetic-and butyric acid, which in turn are removed by methane fermenting bacteria and converted to methane (CH_4) and carbon dioxide (CO_2). The methane in the generated gas accounted for 93 percent of the COD removal in the unit, while a solids balance indicated that only 0.012 g VSS was produced per g COD removed. Due to the low solids production and the initial seeding of the unit was digested sludge no nutrient additions were required during the 518 day period even though the COD:P and COD:N ratios in the feed were as high as 4360:1 and 39:1, respectively. Although a possible heavy metal toxicity, likely the result of high copper concentrations, was observed in the unit, this was eliminated after sulfide addition.

A high percentage of organic matter removal was observed when the hydraulic detention time was maintained above 7 days, but, showed considerably lower removal percentages below this detention time. Increases in organic loading had a substantial effect on the relative organic matter composition of the effluent and the magnitude of the fatty acid fraction showed a pattern inverse to that of the nitrogenous organics. A fixed film model was formulated which indicated that at high substrate concentration the substrate removal rate is proportional to the square root of the substrate concentration and the specific area of the filter medium. A comparison of the biofilm model and the measured effluent concentrations tended to indicate that the substrate removal rate is primarily affected by substrate concentration, specific surface area, flow rate and temperature of the unit.

INTRODUCTION

It has been recognized that biological removal of organics in high strength wastewaters is most economically realized in anaerobic biological systems, since these systems do not have the high energy needs associated with aeration as required in aerobic biological systems (Metcalf and Eddy, 1972). As the cell yield in anaerobic systems is about ten to twenty times lower than that in aerobic systems, the costs of sludge disposal are greatly reduced. During anaerobic fermentation the acid-fermenting bacteria degrade the complex waste to free volatile fatty acids, primarily acetic and propionic acid, which are subsequently converted by the methane fermenting bacteria into methane and carbon dioxide. The generated gas can be combusted to yield valuable energy.

A major disadvantage of the anaerobic fermentation is the sensitivity of the anaerobic bacteria which are inhibited at acidic pH values. In addition, the acid- and methane-fermenting bacteria can experience heavy metal toxicities. Such inhibitions will reduce the biological growth rate and result in their subsequent wash-out. An ideal process is therefore one which is able to retain biological solids independent of the waste flow and maintain sufficient high solids concentration for long periods of time. Such an objective is realized by employing a solid media in the unit to which bacteria can attach. Coulter *et al.* (1954) for example, employed an anaerobic filter filled with rock media to retain solids from an anaerobic digester effluent. Although the majority of the BOD was removed in the preceeding digester, additional removal was observed in the filter. Young and McCarty (1967, 1968, 1969) developed the upflow anaerobic filter in which the anaerobic bacteria are present in a film attached to a rock medium to remove organics in the waste flowing upward through the column. Attachment to the medium results in sludge ages of more than 600 days (Young and McCarty, 1968, 1969) and 150 days (Plummer *et al.*, 1968). The unit can therefore be operated at temperatures substantially below 35°C which decreases the bacterial growth rate while still maintaining a sufficient biomass. Upflow anaerobic filters have been built in England since 1876 to purify sewage but the organic removal was mainly thought to be due to adsorption (Truesdale *et al.*, 1961). The removal of organics in septic tank effluent by bacteria attached to soil particles is based on a similar principle.

The removal efficiencies of the anaerobic filter can be higher than those obtained with anaerobic digesters operated at the same volumetric loading. A comparison of the filter with a digester both maintained at a loading of 1.28 kg COD/m^3 day (80 lb COD/1000 cu ft day) showed that the effluent COD of the anaerobic filter was only one fifth of that of the digester effluent (Foree and Reid, 1973). Tadman (1973) noted that an aerobic filter produced an effluent concentration one tenth of that of an anaerobic digester maintained at the same hydraulic retention time of 2 days. Although Chian and DeWalle (1976) showed that the COD removal in the filter was slightly less than observed in aerated lagoons treating the same waste, the color removal and suspended solids removals, however, are comparable. Moreover, the installation and operating costs of the anaerobic filter are about half of that of an aerated lagoon (Pailthorp *et al.*, 1971).

In a plug flow reactor, the pH decreases initially as a result of the acid fermentation, and then increases in the direction of the flow, due to the biological removal of the generated fatty acids, formation of ammonia and reduction of sulfates. Since the acidic pH in the bottom section of the filter can potentially inhibit the methane fermenting bacteria, substantial amounts of buffer solutions are added to the influent waste stream to prevent such pH decrease. El-Shafie and Bloodgood (1973), for example, added 8,000 mg/ℓ $NaHCO_3$ to the influent having a COD of 11,800 mg/ℓ in order to maintain a pH above 6.5. Young and McCarty (1968, 1969) added $NaHCO_3$ at a concentration of about half of the COD content of the waste, whle Taylor (1972) added 1,000 mg/ℓ $NaHCO_3$ at an influent concentration of 8,800 mg/ℓ COD.

A completely mixed anaerobic filter would not experience the pH decrease observed in plug flow units, since the mixing maintains a fairly uniform pH throughout the depth of the filter. This in turn would eliminate the need for adding costly buffer solutions. In a completely mixed filter, a major part of the effluent is returned and mixed with the influent stream. If the effluent has a sufficient bicarbonate buffer capacity, it is even able to neutralize feed solutions with an acidic pH. Since all of the previous studies with anaerobic filters used once through plug-flow reactors, the present study was conducted to evaluate a completely mixed anaerobic filter.

The high strength acidic wastewater evaluated in this study was a solid waste leachate containing free volatile fatty acids and complex high-molecular-weight carbohydrate-like organics (DeWalle and Chian, 1974) to give a COD of 54,000 mg/ℓ and a pH of 5.4. The fatty acids represented 49 percent of the total COD, while 1610 mg/ℓ carbohydrate, 605 mg/ℓ tannins and 1270 mg/ℓ proteins were also detected. Such leachate is generated in solid waste landfills when infiltrating rainwater allows degradation of primarily cellulosic materials. Collection and treatment of such leachate alleviates the potential problem for groundwater pollution. Due to leaching of metal objects, relatively large amounts of potentially toxic heavy metals were also detected in the leachate used in the present study. The observed concentrations were 2,200 mg/ℓ Fe, 104 mg/ℓ Zn, 18 mg/ℓ Cr, 13 mg/ℓ Ni and 0.5 mg/ℓ Cu.

OBSERVED SUBSTRATE REMOVAL IN FIXED FILM REACTORS

An engineered design of the anaerobic filter requires a knowledge of the substrate removal kinetics in fixed film biological reactors. Such information is obtained when the influent substrate concentration and the hydraulic detention time are varied independantly of each other while the system response is studied. Schulze (1960) noted that the percentage of BOD removal did not change with the increasing influent concentration when an aerobic fixed film reactor was maintained at a constant hydraulic loading. However, when the hydraulic loading was increased and the influent concentration maintained, the percentage removal decreased, indicating that the percentage removal was solely determined by the detention time in the filter. The detention time is a function of hydaulic loading and depth of the filter. The observed results thus follow the first order substrate removal kinetics.

Rinke and Wolters (1970) also varied influent concentration and hydraulic loading independently of each other in aerobic trickling filters and noted that, at a constant hydraulic loading, an increase in influent substrate concentration corresponded to a constant percentage of removal at low organic loadings but showed a decreasing percentage of removal at high loadings. Maintaining a constant organic loading by increasing the hydraulic loading and simultaneously decreasing the influent concentration resulted in a constant amount of substrate removed and a constant percentage substrate removal. Cook and Kincannon (1970) showed, in contrast to Schulze (1960), that at a constant hydraulic loading an increase in influent concentration resulted in a lower percentage substrate removal. Similar to Rinke and Wolters (1970) they noted that at constant organic loading the percentage of removal did not change when the hydraulic loading was increased and the influent concentration was decreased simultaneously. Based on these data one would conclude that recirculation of the effluent to reduce the influent concentration would be beneficial since this would result in a same percentage COD removal with respect to the diluted influent. When the substrate concentration of the effluent is small as compared to the influent concentration, recirculation would then result in a lower actual effluent concentration.

Less variable results have been obtained in evaluating anaerobic filters. Young and McCarty (1968, 1969) showed that increasing the influent concentration at constant but low hydraulic loading resulted in a constant percentage removal but showed a decreasing percentage at high hydraulic loadings. Maintaining the organic loading while decreasing both the influent concentration and the hydraulic detention time resulted in a constant percentage removal at low organic loadings and a decreasing percentage at high organic loadings. The actual effluent concentration, however, was only determined by the organic loading and was independent of influent concentration. Caudill (1968) similarly noted that the COD removal efficiency in an anaerobic filter treating potato starch waste remained at 77 percent when the influent concentration increased from 500 to 1000 mg/COD at constant hydraulic loading. El-Shafie and Bloodgood (1973) also observed a constant percentage removal independent of the influent concentration at a given hydraulic loading. Jennett and Dennis (1975) found that at a constant organic loading of 3.5 kg COD/m^3 day (220 lb COD/1000 cu ft day) the percentage removal decreased from 98 percent to 95 percent and 94 percent respectively when the influent concentration decreased from 16,000 mg/ℓ to 8,000 mg/ℓ and 4,000 mg/ℓ. The observation that the actual effluent concentration also decreased, would indicate that recirculation could result in slightly lower effluent concentrations.

The above considerations are important in evaluating the effect of recirculation on substrate removal efficiency as practices in the present study. Based on fundamental considerations, both Schulze (1960) and Germain (1964) concluded that recirculation would have no effect on organic matter removal. However, both Eckenfelder (1961) and Gallar and Gotaas (1964), using a large number of actual aerobic trickling filter plant data, concluded that recirculation resulted in a larger percentage substrate removal possibly due to the inoculation of the incoming sewage with bacteria present in the effluent. Several studies compared treatment efficiency before and after recirculation was practiced and generally noted an improvement in effluent quality. Moore *et al.* (1950) noted that a recirculation ratio of one improved the BOD removal from 85 percent to 93 percent at an influent BOD of 240 mg/ℓ. Using a similar recirculation ratio Hanumanula (1969) noted that the BOD removal increased from 62 percent to 91 percent at an influent BOD of 330 mg/ℓ. Oleszkiewics (1974) showed that recirculation is especially beneficial at high influent substrate concentrations due to better aeration of the liquid film and the elimination of substrate inhibition. He observed an improvement of the removal from 30 percent to 85 percent at a recirculation ratio of 5 using an influent COD of 3,000 mg/ℓ.

SIMULATION OF SUBSTRATE REMOVAL IN BIOFILMS

The substrate removal kinetics in fixed film biological systems can either be described in terms of substrate concentrations existing in the bulk liquid phase or simulated substrate concentrations in each layer of the biofilms, the sum of which predicts the response of the entire film. Kornegay and Andrews (1969) and Young and McCarty (1968, 1969) used the former approach; the latter authors introduced a substrate gradient factor defined as the ratio of the concentration at the liquid-biofilm interface to the effective concentration in the biofilm. As a result, the calculated apparent half velocity concentrations are several times larger than would be obtained if all bacteria were complete dispersed. Recent studies however, generally use the second approach in which the process of substrate diffusion and bacterial uptake are simulated for each of the successive layers of the biofilm; the present study used a similar approach.

In a biological film reactor at steady state, a mass balance within the film can be made by equating:

$$\text{input} - \text{output} = \text{uptake} \qquad (1)$$

According to Fick's law of molecular diffusion the mass transfer rate dF/dt through a surface area A is proportional to the concentration gradient of the substrate S at the interface:

$$\frac{\partial F}{\partial t} = - A\, D_s \frac{\partial S}{\partial z} \qquad (2)$$

$\frac{\partial F}{\partial t}$ = rate of mass transfer at interface (mass/time)

D = diffusion coefficient (length^2/time)

$\frac{\partial S}{\partial z}$ = substrate concentration gradient (mass/length^4)

z = depth of biofilm starting from liquid-film interface (length)

A = surface area of biofilm (length^2)

The biological uptake within the biological layer can be expressed as:

$$\frac{dS_z}{dt} = \frac{US_zX}{K_s + S_z} \qquad (3)$$

$\frac{dS_z}{dt}$ = rate of substrate uptake (mass/length^3 time)

U = maximum substrate removal rate $\left(\frac{\text{mass of substrate}}{\text{mass of biomass}\cdot\text{time}}\right)$

S_z = substrate concentration at depth z (mass/length^3)

X = biomass concentration within the biolayer (mass/length^3)

K_s = half velocity concentration (mass/length^3)

By making a material balance between a differential distance within the biolayer using equations (1), (2) and (3), it results in the following equation for a unit cross sectional area:

$$\frac{d^2S_z}{dz^2} = \frac{1}{D_x} \cdot \frac{US_zX}{K_s + S_z} \qquad (4)$$

which states that the second derivative of the substrate concentration with respect to z is dependent on both the substrate and biomass concentration. When axial dispersion becomes important the term $v \cdot \frac{\partial S}{\partial z}$ will have to be added to the right hand side of Equation (4). However, since the filter media in the present study consists of long curved channels, this term can be omitted.

Equation (4) is a second order non-linear differential equation. As such it does not have a simple solution. However the equation can be solved when S_z is either much larger or much smaller than K_s (Hang and McCarty, 1971). When S_z is much larger than K_s Equation (4) reduces to a zero order kinetic equation;

$$\frac{d^2S_z}{dz^2} = \frac{UX}{D_s} \qquad (5)$$

which can be integrated for a unit cross sectional area, and the mass transfer rate at the interface becomes:

$$\frac{dF}{dt} = UXh \qquad (6)$$

h = thickness of biofilm (length)

Since for a given waste, U and X are not expected to vary greatly, equation (6) would indicate that the rate is independent of substrate concentration but directly proportional to surface area and thickness of the biolayer. In such a situation the decrease of substrate within the biofilm is small as compared to the concentration at the interface so that the rate of substrate utilization per unit of biomass is approximately the same as if the solids were evenly dispersed throughout the liquid. According to Pirt (1973) and Saunders and Bazin (1973) the thickness of the biolayer can be approximated by

$$h = \frac{2D_s \cdot S_b}{UX} \qquad (7)$$

S_b = substrate concentration in bulk liquid (mass/length^3)

However, equation (7) was derived based on the boundary conditions of zero substrate concentration at the interface of the biolayer and the solid support; it therefore violates the constraint that S_z is much larger than K_s and is therefore only an approximation. Since D_s, U, and X are not expected to vary to a great extent for a given substrate, Equation (6) can therefore be further modified to indicate that the rate of substrate removal per unit reactor volume is related to the specific surface area, A/V, and the square root of the bulk substrate concentration:

$$\frac{dF}{Vdt} = k_1 \cdot \frac{A}{V} \cdot \quad S_b \qquad (8)$$

k_1 = coefficient based on zero order kinetics (mass$^{\frac{1}{2}}$/length$^{\frac{1}{2}}$·time)

V = reactor volume (length^3)

An equation similar to equation (8) was also used by DeWalle and Chian (1976) to describe the rate of biological regeneration of activated carbon particles due to the presence of activated sludge solids. It is realized that at very high substrate concentrations the rate of substrate removal will be independent of the substrate concentrations due to the zero order kinetics of the reaction. In that case the rate of substrate removal will only be dependent on the specific surface area in the reactor.

When S_z is much smaller than K_s, equations (4) reduces to a first order kinetic equation:

$$\frac{d^2S_z}{dz^2} = \frac{UXS_z}{D_s \cdot K_s} \qquad (9)$$

Which after integration yields the mass transfer rate equation at the interface:

$$\frac{dF}{dt} = S_b \quad \frac{D_s \; UX}{K_s} \qquad (10)$$

Since D_s, U, X and K_s are not expected to vary greatly with a given substrate, Equation (10) reduces to

$$\frac{dF}{Vdt} = k_2 \cdot \frac{A}{V} \cdot S_b \qquad (11)$$

k_2 = coefficient based on first order kinetics (length/time)

The equation indicates that the rate of substrate removal per unit reactor volume is related to the specific surface area of the biofilm and the bulk substrate concentration, but is independent of film thickness. A similar equation has been given by Atkinson and Daoud (1968) for large film thickness. Equations (8) and (11) should be used in small successive sections in plug flow anaerobic filter columns. However, since such detailed data are generally not available, both equations can be used with respect to the whole column while S_b is substituted by the effluent concentration of the column.

Additional resistance to mass transfer from the bulk liquid to the liquid-biofilm interface is caused by the liquid film adjacent to the biofilm. The thickness of this layer can be described by the Nusselt (1916) equation:

$$\delta = \left[\frac{3\ \nu\ Q}{\rho\ g\ W}\right]^{1/3} \qquad (12)$$

Q = flow rate (length^3/time)
ν = viscosity (mass/time·length)
ρ = density of liquid (mass/length^3)
g = gravitational constant (length/time^2)
W = width of film (length)
δ = thickness of film (length)

Since the mass transfer rate decreases with increasing liquid film thickness in the laminar sublayer, the flux of substrate would also be proportional to the flow rate to the power 1/3. This agrees with the analysis by Takeshi *et al.* (1972) that the mass transfer coefficient K_L for laminar flow can be expressed as:

$$K_L = kQ^{1/3} \text{ for Re} < 10 \text{ and} \qquad (13)$$

$$k_L = kQ^{1/2} \text{ for Re} > 10 \qquad (14)$$

Both equations (8) and (11) illustrate the importance of the specific surface area, A/V, of the fixed film reactor. Based on similar considerations Ames *et al.* (1962) stated that the substrate removal was proportional to the specific surface area of the media. Lamb and Owen (1970 came to the identical conclusion. For the above reasons, a filter medium with a relatively high specific surface area of 206 m^2/m^3 (63 ft^2/ft^3) was selected for the present study.

MATERIALS AND METHODS

The laboratory scale anaerobic filter column was constructed of Plexiglas with an overall height of 246 cm and 20.2 cm OD (Figure 1). The height of the filter medium in the column was 199 cm and comprises a volume of 54.6 liter (1.93 cu ft). A head space of 1.4 liter is provided at the top of the medium while the inlet section is 2.8 liter. A solids collection device, installed at the end of the second period in Phase II, is located at the bottom of the column and has a volume of 3.8 liter. A recirculation surge vessel with a volume of 5.2 liter provides the separation of the effluent stream and the recirculation stream. The latter is subsequently used to dilute the incoming leachate and raise its pH. The total volume of the column is therefore 67.8 liter of which 54.6 liter or 81 percent contains the filter medium to which the bacteria are attached.

The medium in the column consists of plastic "Surpac" slabs (Dow Chemical Midland, MI) while additional plastic strips were placed between each sheet. The plastic material has a specific density of 1.45 g/cm^3. As the average thickness of the slab is 0.57 mm, on the basis of 100 measurements, the specific surface of the plastic material itself is therefore 3490 m^2/m^3 (1067 ft^2/ft^3). The specific surface area of the media per unit column volume is 206 m^2/m^3 column volume (63 ft^2/ft^3 column volume); the total surface area in the column is therefore 11.3 m^2 (121.6 ft^2) and only 6 percent of the column volume is taken up by the plastic material resulting in a porosity of 94 percent. A comparable study by Young and McCarty (1968, 1969) used smooth quartzite stones with a porosity of only 42 percent and a specific surface area of 114 m^2/m^3 column volume (37.5 ft^2/m^3 column volume) as estimated from data provided by Truesdale *et al.* (1961).

The leachate employed in this study was obtained from a lysimeter filled with solid waste to which simulated rainwater was added (Chian and DeWalle 1976). After collection from the lysimeter, the leachate was refrigerated

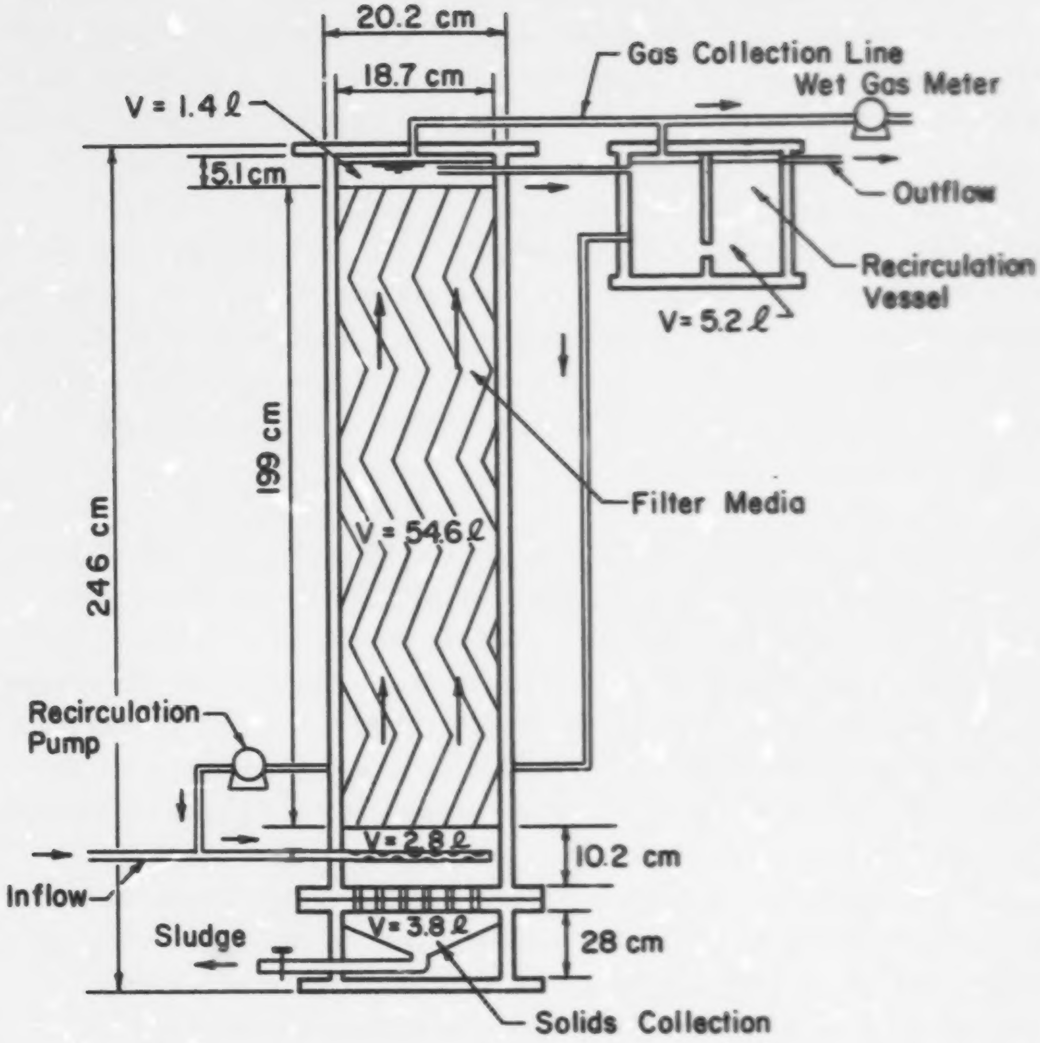
20.2 cm
18.7 cm
Gas Collection Line
Wet Gas Meter
V = 1.4 ℓ
5.1 cm
Outflow
Recirculation Vessel
V = 5.2 ℓ
199 cm
246 cm
Filter Media
V = 54.6 ℓ
Recirculation Pump
V = 2.8 ℓ
10.2 cm
Inflow
Sludge
V = 3.8 ℓ
28 cm
Solids Collection

Figure 1. The Completely Mixed Anaerobic Filter

and fed from a 10 liter container into the anaerobic filter using an electrolytic gas cell, in which the O_2 and H_2 generated were used to expand a bladder located in the leachate container to displace its content. Due to the formation of iron hydroxide solids, the leachate could not be fed with regular positive displacement pumps without excessive wearing.

RESULTS AND DISCUSSION

Studies on the effectiveness of the anaerobic filter in treating high strength leachate from the lysimeter were conducted for a period of 518 days starting July 3, 1973. During Phase I of the study, which lasted 218 days the different start-up procedures and pH stabilities of the unit were tested, while in Phase II which lasted 250 days, the various operational difficulties of the completely mixed unit were evaluated. Phase III, which lasted 50 days, was used to study the effluent characteristics as affected by organic loading. A summary of the different steps is given in Table 1.

Start-up of the Anaerobic Filter

The start-up of the anaerobic filter was tested during the early stage of the Phase I study. It was noted that when the undiluted leachate was passed through the unit without seeding no significant biological degradation would occur for a 33 day period when the unit was operated at a detention time of 42 days. Also, no biomass would develop on the filter media, even when the pH of the incoming leachate was adjusted with sodium hydroxide from 5.8 to 7.0, i.e., the minimum required pH for methane fermentation. The filter was therefore emptied and the bottom section was seeded with 1 liter of digested sludge containing a total 25 g solids while the column was filled with the leachate diluted to one tenth of its strength with distilled water. Thereafter the unit was fed 1.6 liter of the diluted leachate to give a detention time of 42 days. A high initial gas production was observed which gradually decreased (Figure 2a). Increasing the influent concentration by using a lower dilution ratio resulted in increasing amounts of gas being generated in the unit as a result of the microbial methane fermentation. However, when the undiluted leachate was fed, inhibition was observed as the gas production ceased completely. A larger quantity of 2 liter of digested sludge, containing 50 g solids, and a less rapid increase in the influent concentration, however, resulted in a satisfactory gas production, approaching the theoretical amount as calculated from the COD removal

Table 1. Different Phases and Experimental Conditions During the Anaerobic Filter Study

Phase	Duration (days)	Period	Duration (days)	Hydraulic Detention Time (days)	Leachate Feeding Rate (ℓ/d)	Combined Influent Flow Rate (ℓ/d)	Recirculation Ratio	Leachate Influent COD (mg/ℓ)	Experimental Conditions
I	218	1a	1-33	42	1.6	32.4	1:20	62,000	no pH adjustment; no seeding
		1b	33-64(31)	42	1.6	32.4	1:20	62,000	pH adjustment to 7; no seeding
		2a	64-103(39)	42	1.6	32.4	1:20	6,200-62,000	seeding 1ℓ sludge; decreasing dilution
		2b	103-146(43)	42	1.6	32.4	1:20	6,200-31,000	seeding 2ℓ sludge; decreasing dilution 1:10 to 1:2
		3a	146-188(42)	42	1.6	32.4	1:20	27,000	feed 1:2 diluted leachate
		3b	188-200(12)	42/7	1.6/9.7	32.4/40.5	1:20/1:4.2	27,000	first shockload
		3c	200-218(18)	42/4.25	1.6/16	32.4/46.8	1:20/1:2.9	27,000	second shockload
II	250	1a	218-291(73)	42	1.6	32.4	1:20	27,000	start of extensive monitoring
		1b	291-293(2)	42/3.0	1.6/22.7	32.4/53.5	1:20/1:29	27,000	Third shockload
		1c	293-298(5)	42	1.6	32.4	1:20	27,000	extensive monitoring
		1d	298-362(64)	42	1.6	32.4	1:20	19,500	gradual toxicity, Na_2S
		2	362-398(36)	42	1.6	32.4	1:20	19,500	solids collection device installed
		3	398-432(35)	42	1.6	32.4	1:20	19,500	between period 2 and 3
		4	432-467(35)	74	0.9	31.7	1:35	39,000	doubling of leachate concentration
III	50	1	467-497(30)	74	0.9	31.7	1:35	32,000	kinetic analysis
		2	497-512(15)	17.5	4.0	34.8	1:8.7	32,000	kinetic analysis
		3	512-517(5)	7.5	9.1	39.9	1:4.4	32,000	kinetic analysis

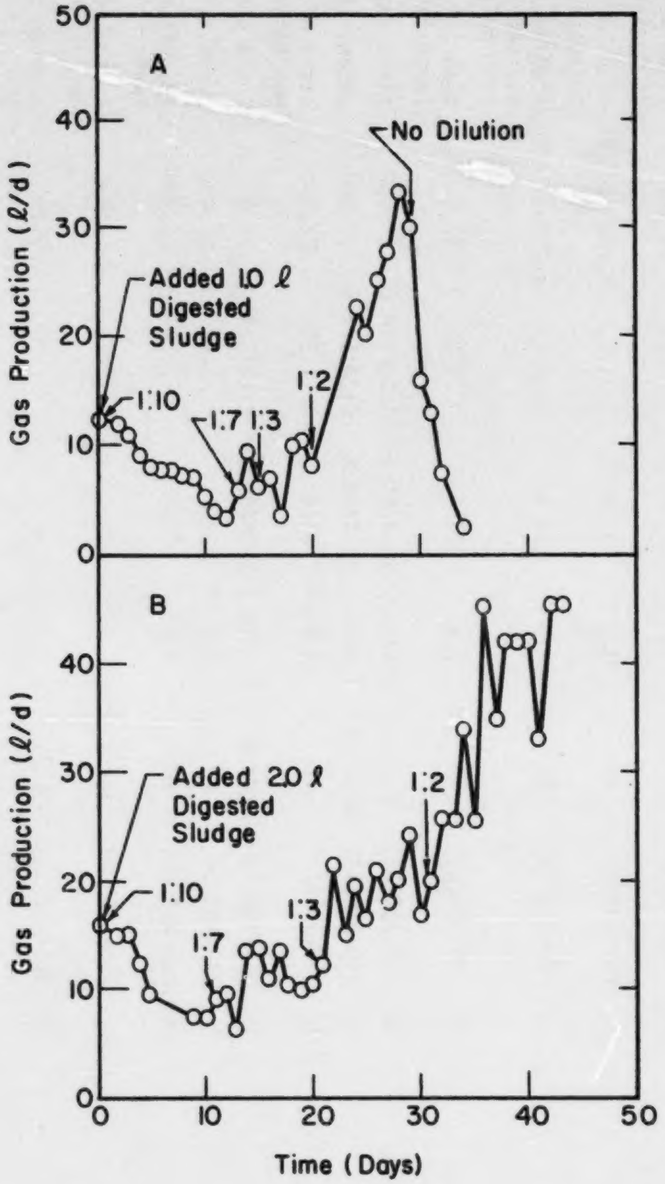

Figure 2. The Startup of the Anaerobic Filter

(Figure 2b), after 43 days. In order to prevent possible further inibition, a new batch of leachate was fed to the unit at a 1:2 dilution (1 part of feed to 1 part of dilution water) resulting in an influent COD of 27,000 mg/ℓ. Similarly to the present study Young and McCarty (1968, 1969) noted that about 40 days of operation were required to reach equilibrium conditions when two additions of 30 g volatile solids from a sludge digester were used to start the filter. Adding 30 g of digested sludge to the bottom section of an aerobic filter, Jennett and Dennis (1975) noted that only 20 days were required to reach equilibrium conditions.

Recirculation Ratio

After a 42 day operating period, equivalent to one volume turnover, the required recirculation ratio was studied. Approximately 63 percent of the constituents in the initial leachate batch would be displaced after one volume turn over for a completely mixed reactor. Initially, a 1:20 recirculation ratio was arbitrarily selected at the beginning of the study. A recirculation ratio of 1:20 was defined as 1 part of feed to 19 parts of effluent to results in a total volume of 20 parts. A titration curve of the effluent as shown in Figure 3a, indicates that the highest buffering capacity of the effluent is observed at a pH of 6.2, shile less is available at the actual effluent pH of 7.2. The pH of the inflection point at 3.9 reflects the presence of both bicarbonates and fatty acids. If only bicarbonate had been present, the pH of the inflection point would have been close to 4.3. Because of this observed shape of the effluent titration curve, five parts of effluent are required to increase the pH of the influent to 7.0, thus, requiring a minimum ratio of 1:6 (Figure 3b). In order to operate the unit safely and well-mixed the ratio of 1:20 was maintained by using a recirculation flow rate of 30.8 ℓ/d, resulting in a complete mixing of the unit every 1.8 days as calculated for the column volume subject to mixing. Since the time required for mixing was short as compared to the hydraulic detention time, i.e., 1.8 days versus 42 days, the unit can be considered completely mixed. As a result of the recirculation, the vertical upflow rate in the unit was 1.1 m/d.

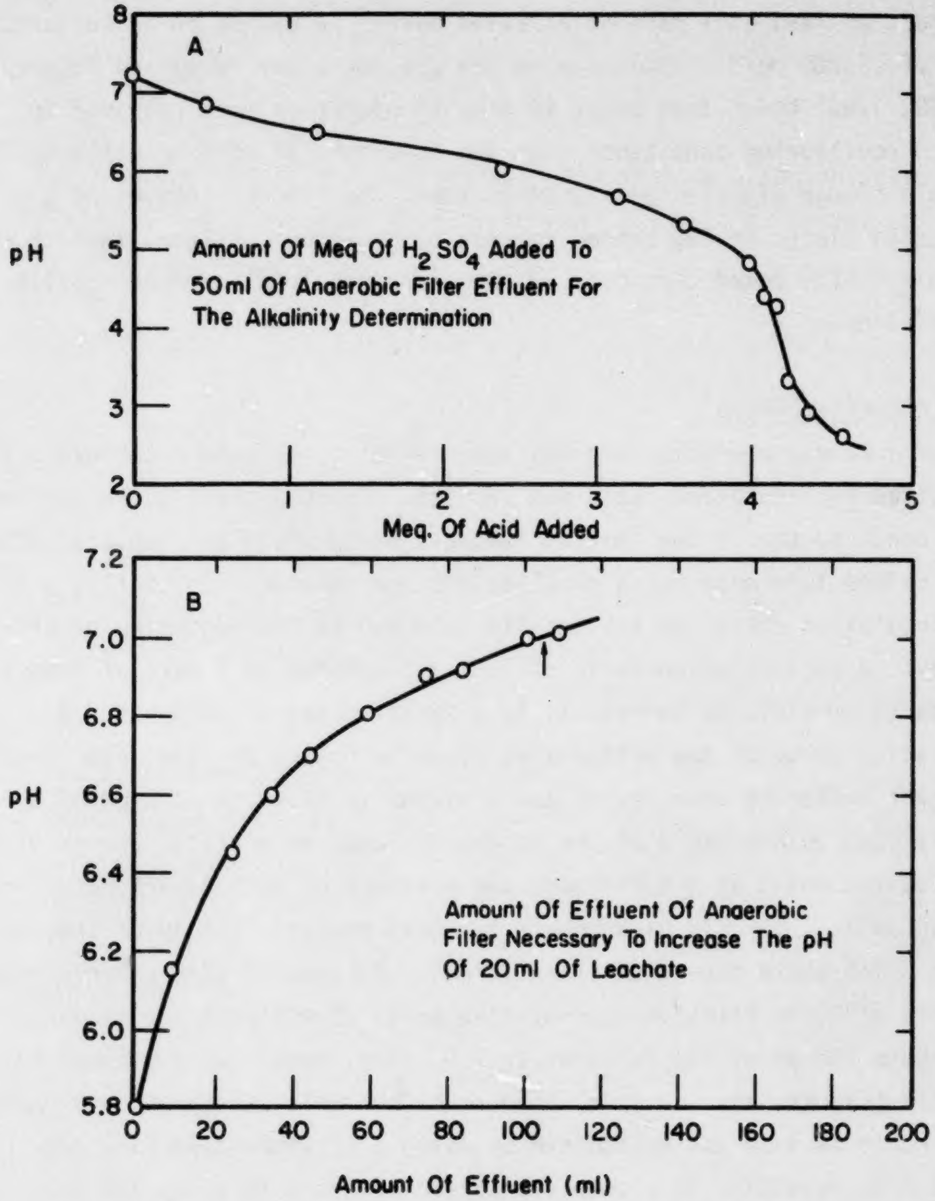

Figure 3. Determination of the Minimum Required Recirculation Ratio

Shockloading

Before a more extensive monitoring was initiated, the ability of the anaerobic filter to withstand shockloads was studied. When the detention time, based on feed stream flow alone, was reduced from 42 days to 7 days for a one-day period, only a small change in the pH was observed (Figure 4a and b). Since the recirculation flowrate was kept constant, the recirculation ratio experienced a decrease. The pH decreased to 6.9 when the detention time was reduced to 4.25 days for a one-day period (Figure 4c and d). A larger shockload was conducted in Phase II, 73 days after the more intensive monitoring of the unit had started. The detention time was reduced to 3 days for a two day duration which also caused a similar lowering of pH values (Figure 4e and f). The gas production did not show a corresponding increase, as high concentration of organics were present in the effluent of the unit (Figure 5a) which reduced the organic removal efficiency to 54 percent. The high COD values corresponded with high concentrations of fatty acids (Figure 5b), aromatic hydroxyls and carbohydrates (Figure 6a). The large differences in the values for the filtered and unfiltered COD may indicate that substantial quantities of solids were resuspended at the higher flow rates. This was also indicated by the suspended solids (SS) analysis (Figure 7b). As most of the phosphates in the unit are present as suspended solids, a similar pattern as the SS was observed (Figure 7c). Since fatty acids contribute to the alkalinity, an increase parallel to the fatty acids was observed (Figure 7e). After the detention time was restored back to 42 days after the two days shockload, the effluent COD and SS concentrations returned to values only slightly higher than those observed before the shockload. It is realized that at short detention times the flow regime of the unit tends to depart from a completely mixed pattern and approaches that of a plugflow, since at a three day detention time, the content is only mixed 2.7 times during one volume turnover. Based on these tests it was concluded that the buffer capacity of the unit is sufficient to prevent large pH depressions at relatively short detention times. However, at detention times as short as three days a large portion of the organics leave the unit in the effluent stream. Further-

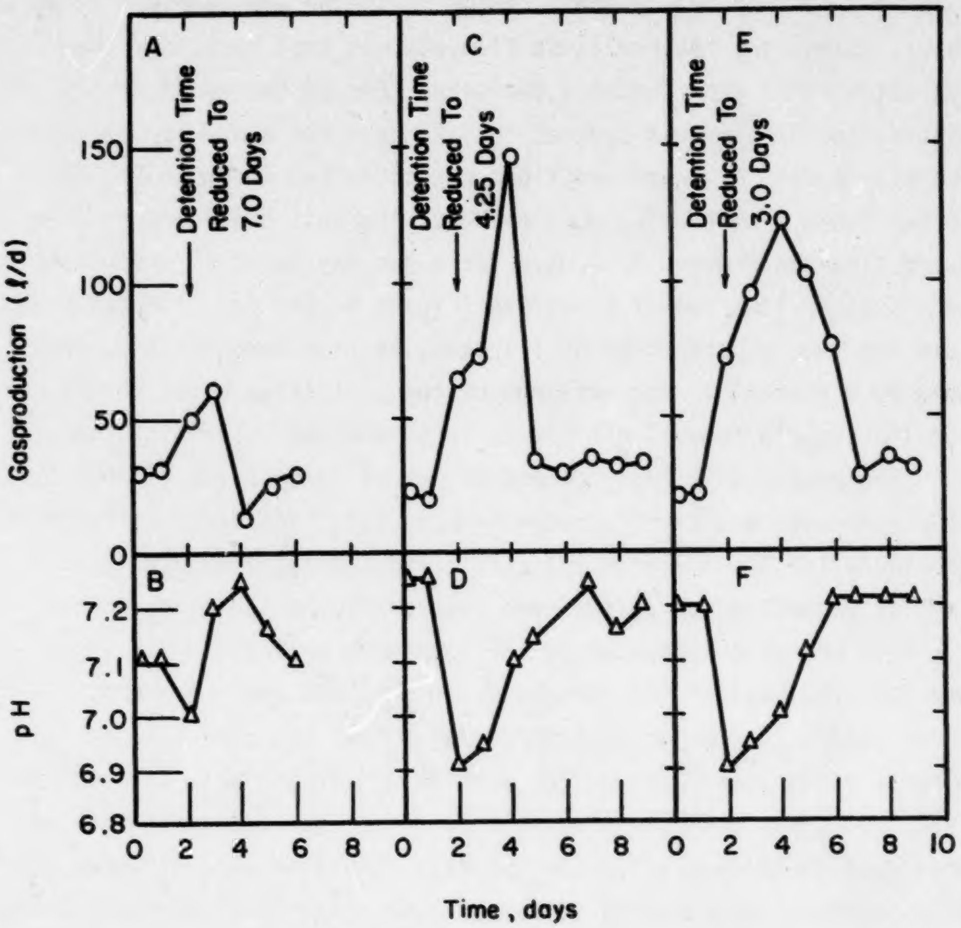

Figure 4. Stability of the Anaerobic System under Different Shockloads

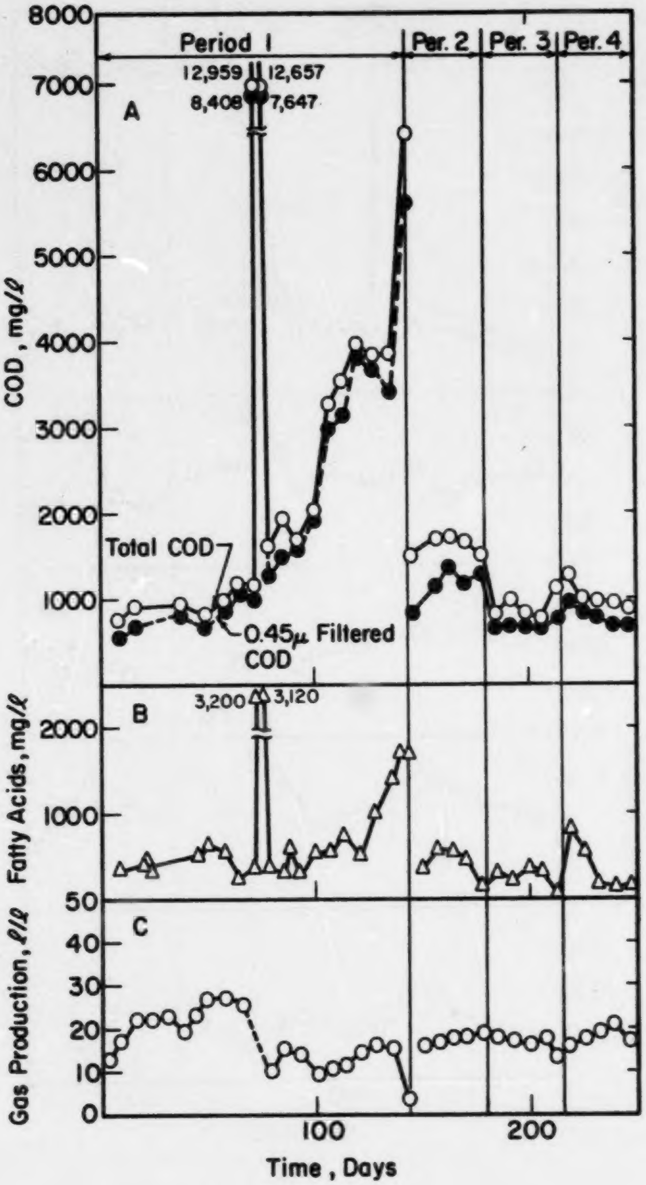

Figure 5. Effluent Quality During Phase II as Measured by COD, Fatty Acids and Gas Production

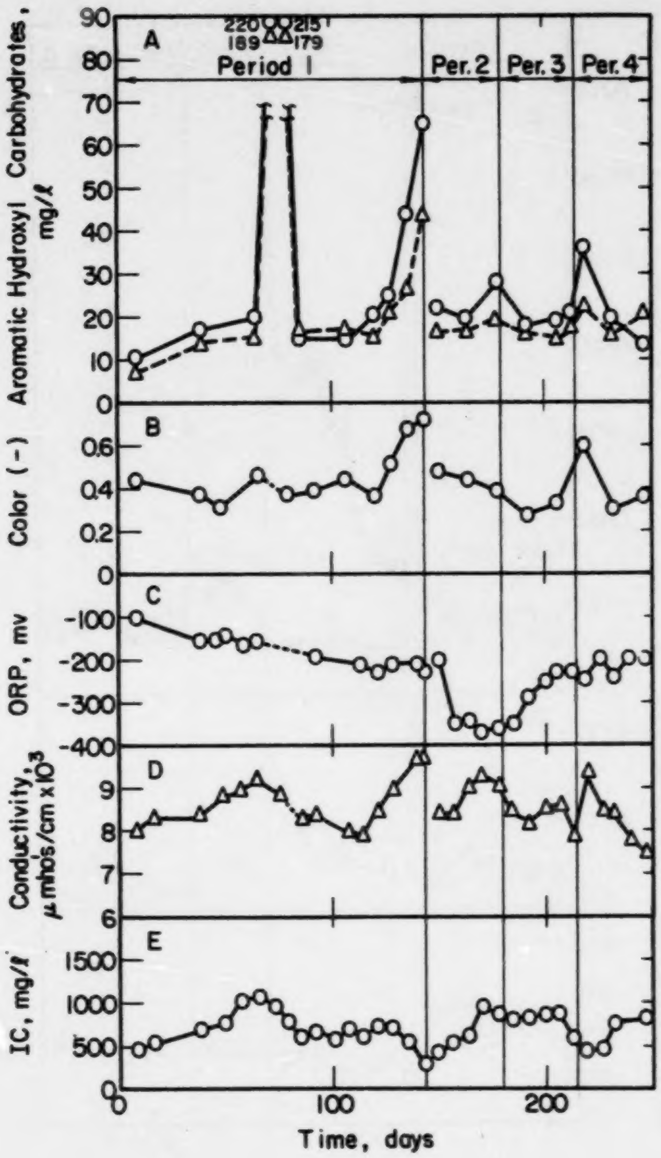

Figure 6. Effluent Quality During Phase II as Measured by Carbohydrates, Aromatic Hydroxyls, Color, ORP, Conductivity and Inorganic Carbon

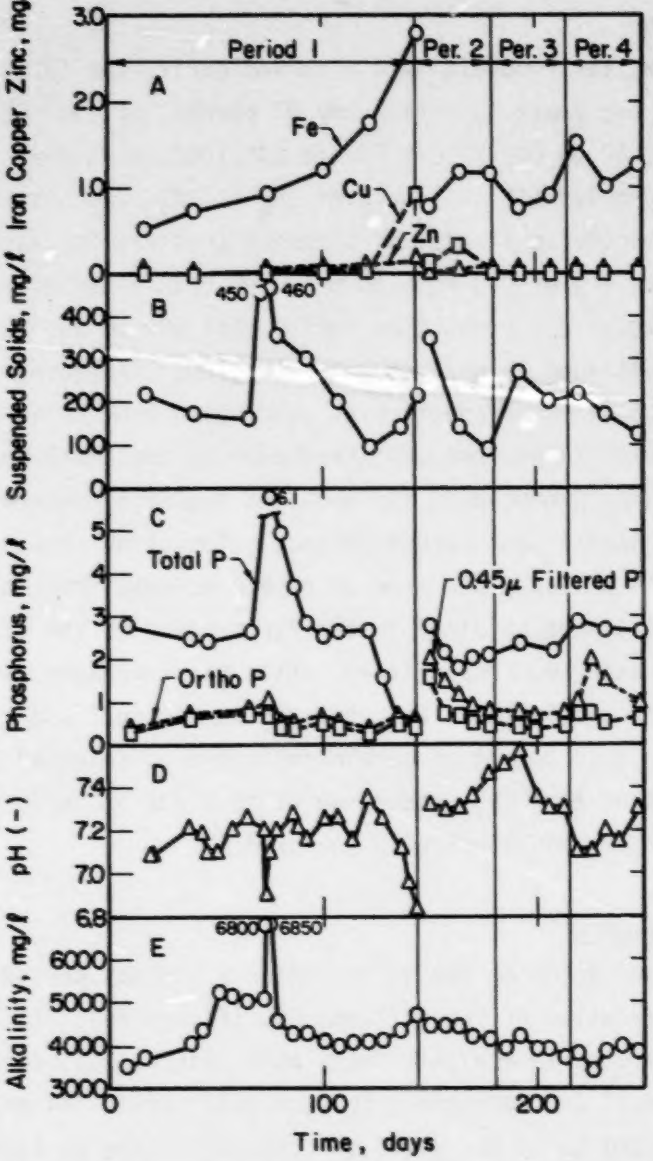

Figure 7. Effluent Quality During Phase II as Measured by Heavy Metals, Suspended Solids, Phosphorus, pH and Alkalinity

more high concentration of suspended solids are detected in the effluent at such short detention times.

Gas Production

High organic matter removals were observed during the first 60 days of monitoring in the Phase II period and 97 percent of the COD was removed at a rate of 0.62 kg COD/m^3 day (39 lb COD/1000 cu ft day) (Figure 5a). As the oxygen equivalent of 1 mole of CH_4 is $2O_2$, 22.4 liter of methane are therefore produced at 0°C and standard pressure for each 64.4 g COD removed. Thus, 1 g of COD removed produces 0.38 liter of methane gas at 25°C. The average gas production during that period was 23.3 ℓ/ℓ influent, and the gas contained 78 percent methane. This corresponds to 89 percent of the theoretical gas production as calculated from total COD removals. The difference of 11 percent was attributed to the small amount of biological solids produced in the unit and organics removed by physical processes. A theoretical carbon balance calculation showed that 1.75 liter of gas is produced per gram of carbon removed from solution. The leachate and effluent obtained in the first phase of the study had COD/TOC ratios of 3.5 and 2.8, respectivley, while the inorganic carbon concentration present in the influent and effluent was 10 mg/ℓ and 750 mg/ℓ, respectively. This amount of carbon removed from solution would theoretically correspond to a gas production of 23.2 ℓ/ℓ of influent which was 99 percent of the amount actually measured.

Heavy Metal Toxicity

Continuing observation of the filter after a 100 day period showed a gradual deterioration of the effluent COD (Figure 5a). This was subsequently reflected in a higher fatty acid (Figure 5b), carbohydrate and aromatic hydroxyl concentrations (Figure 6a). After 144 days, the COD removal decreased to as low as 64 percent, while the pH decreased below 6.8 (Figure 7d) which effectively reduced the methane fermentation (Figure 5c). Analysis of the effluent showed a gradual increase in soluble (0.45 μ filtered) heavy metals with maximum Fe, Cu and Zn concentrations of 2.8, 0.9 and 0.2 mg/ℓ, respectively (Figure 7a), indicating that heavy metal toxicity may have inhibited the anaerobic fermentation. The metals were mostly present in the suspended form and the dissolved iron, for example, represented only 9 percent of the total iron content.

Lawrence and McCarty (1965) and Mosey *et al.* (1971) showed that the concentration of soluble heavy metals was determined by the amount of sulfide present in the unit to form insoluble sulfide precipitates. Since iron is the metal generally present in highest concentrations, the ferrous sulfides in the unit constitute a sulfide reservoir to precipitate the more toxic and less soluble heavy metals such as copper, zinc and nickel. Based on the measurement of soluble sulfides in digesters, Mosey and Hughes (1975) concluded that a 50 percent decrease in gas production would occur at concentrations of 10^{-4} mg/ℓ Zn^{++}, 10^{-7} mg/ℓ Cd^{++}, 10^{-12} mg/ℓ Cu^{+} and 10^{-16} mg/ℓ Cu^{++}. Inhibition during shockloads of short duration occurs at much higher soluble heavy metal concentrations of 0.5 mg/ℓ Zn^{++}, 1 mg/ℓ Cd^{++}, 10^{-7} mg/ℓ Cu^{+} and 10^{-8} mg/ℓ Cu^{++}. Kirsch and Sykes (1971) reported that at a total zinc concentration of 100 mg/ℓ and a soluble concentration of 1.5 mg/ℓ, gas production was inhibited. However, failure did not occur when the zinc was fed as zinc sulfate as a result of which the soluble zinc concentration never exceed 0.4 mg/ℓ. None of the studies noted a toxicity due to iron.

Since the present study noted significant concentration of copper, one of the most toxic elements, the observed inhibition could well be due to this element. Similar to Lawrence and McCarty (1965) it was noted that the initial deterioration of the effluent COD was not caused by a higher fatty acid concentration, indicating that the acid fermenting bacteria were more affected by the inhibiting substance than the methane bacteria. A limited number of analyses indicated that approximately half of the sulfate concentration of 550 mg/ℓ, in the 1:2 diluted leachate was removed in the unit by reduction and precipitation. Stoichometric amounts of sulfide would only precipitate 9 percent of the iron removed in the unit, indicating that the majority of the iron at neutral pH values would be precipitated as carbonates and hydroxides; a conclusion similar to that reached by Mosey and Hughes (1975). Unlike the metal-sulfide precipitates, the carbonate precipitates are very pH sensitive and dissolve at low pH values. This may explain the increase in Zn and Cu concentrations between 120 and 144 days (Figure 7a). These results may indicate that initially the acid fermenting bacteria were partially inhibited by metals resulting in higher effluent COD (Figure 6a). This was subsequently followed by inhibition of the methane bacteria, as a result of which the fatty acid concentration gradually increased (Figure 5b). Since less bicarbonate alkalinity was formed, the pH in the unit started to decrease, which in turn dissolved additional heavy metal precipitates; the solubilized metals when resulted in further inhibition. The results further show that the values of pH and conductivity reflect increases in the fatty acid concentration. The earliest warning of possible metal toxicity, however, is given by a gradual decrease in total gas production and an increase of the effluent COD. To reduce the observed toxicity half of the column volume was drained and filled with tap water to reduce the inhibiting substances. Since metal toxicity was suspended, their concentration was decreased by addition of 75 mg/ℓ Na_2S to the column content, while a similar concentration was added to the influent for the next 18 days. After these operational changes the observed effluent quality during the second monitoring period of Phase II improved greatly while the gas production, the organic matter removal, and the bicarbonate alkalinity increased gradually. The sulfide additions caused a decrease in ORP values while reducing the heavy metal concentrations (Figure 6c). Furthermore, no H_2S odor was detected also indicating that the toxicity was caused by metals.

In subsequent studies with the same anaerobic filter using a different feed, experiments were made to study the effect of hydraulic loading on the removal of heavy metals. Four different loadings were evaluated in duplicate during which the metal concentrations in samples withdrawn from the different sampling ports along the filter were measured. Using the effluent and influent concentrations, the removal percentages can be calculated. The analytical results in Figure 8 show that the removal of most metals is 68 percent or higher, except for copper and cadmium. The

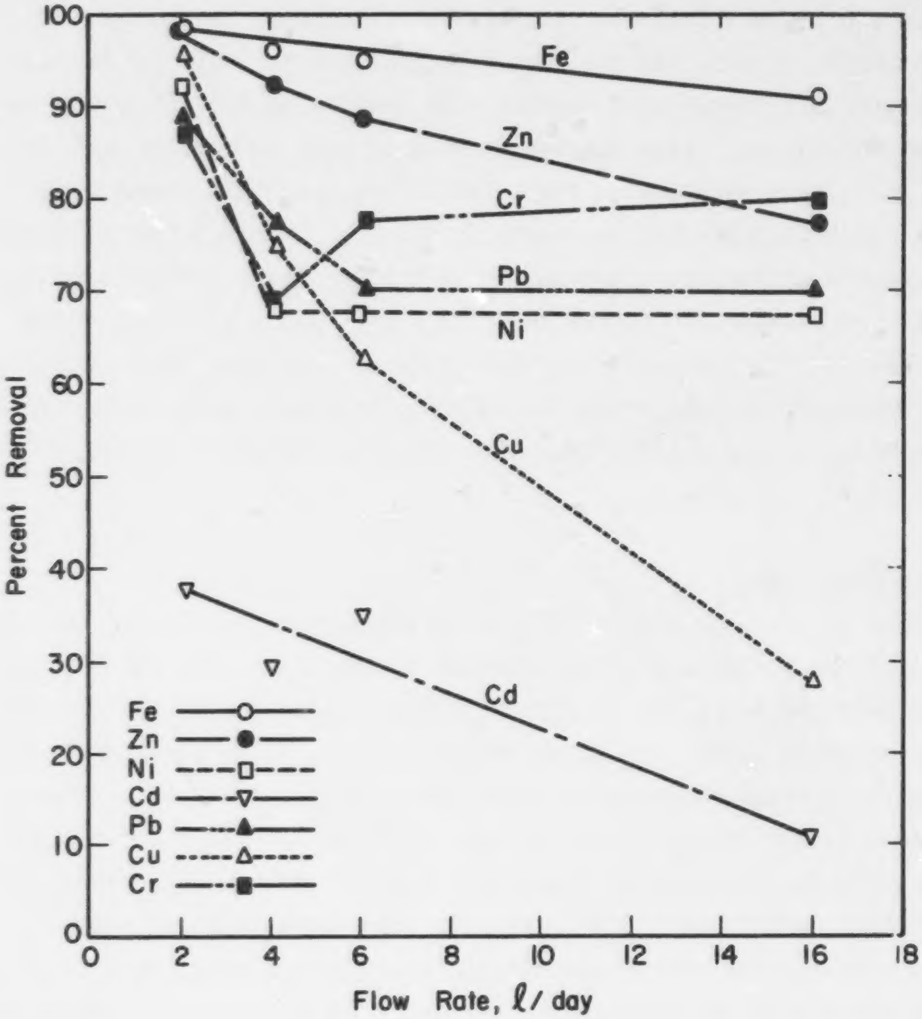

Figure 8. Effect of Increasing Hydraulic Loadings on Percentage Removal of Different Heavy Metals

percentage removal generally decreases with increasing flowrates with the exception of chromium, which element is likely present as the chromate anion and not as the cation. Iron showed the highest removals while it also had the highest initial concentrations. Cadmium had the lowest removals while it also had the lowest initial concentration. The most rapid decrease in percentage removal with increasing feed flowrates was observed for copper. Thus at high loadings copper is removed to a lesser extent than the other metals, again indicating that this element may cause a metal toxicity in the anaerobic filter. Although the percentage metal removal decreases at increasing flowrates, the absolute quantity of metals increases with increasing flowrates. Since a large portion of the metals form insoluble sulfide, carbonate and hydroxide precipitates, which coagulate and settle out in the unit, increased metal concentrations were observed in the sludge drawn from the bottom portion of the filter (Figure 9).

Nutrient Requirements

Comparison of effluent and influent total phosphorus (P) showed that 55 percent of the concentration was removed in the unit. The COD:P ratio of the influent, however, was as high as 4360:1 indicating that a phosphorus limitation could occur. Young and McCarty (1968, 1969) selected a 470:1 ratio using a protein-carbonate waste and a fatty acid waste. McCarty and Speece (1963) measured that a feed COD:P ratio of as high as 2200:1 was feasible in an anaerobic digester fed with fatty acids. Foree and Lovan (1971) maintained a 500:1 ratio in their unit treating press brewery liquor. The latter investigators noted that about half of the applied phosphorus was utilized in the unit. In a subsequent investigation using the same unit they maintained a COD:P ratio of 1000:1 using a wastestream similar to the one used in the present study (Foree and Reid, 1973). They noted that 96 percent of the applied phosphorus was removed, indicating that only slightly higher ratios are feasible. Although the waste in the present study was fed to the units without nutrient suppliments, a significant amount of phosphorus of 1328 mg was initially introduced in the unit through the anaerobic sludge used to feed the unit.

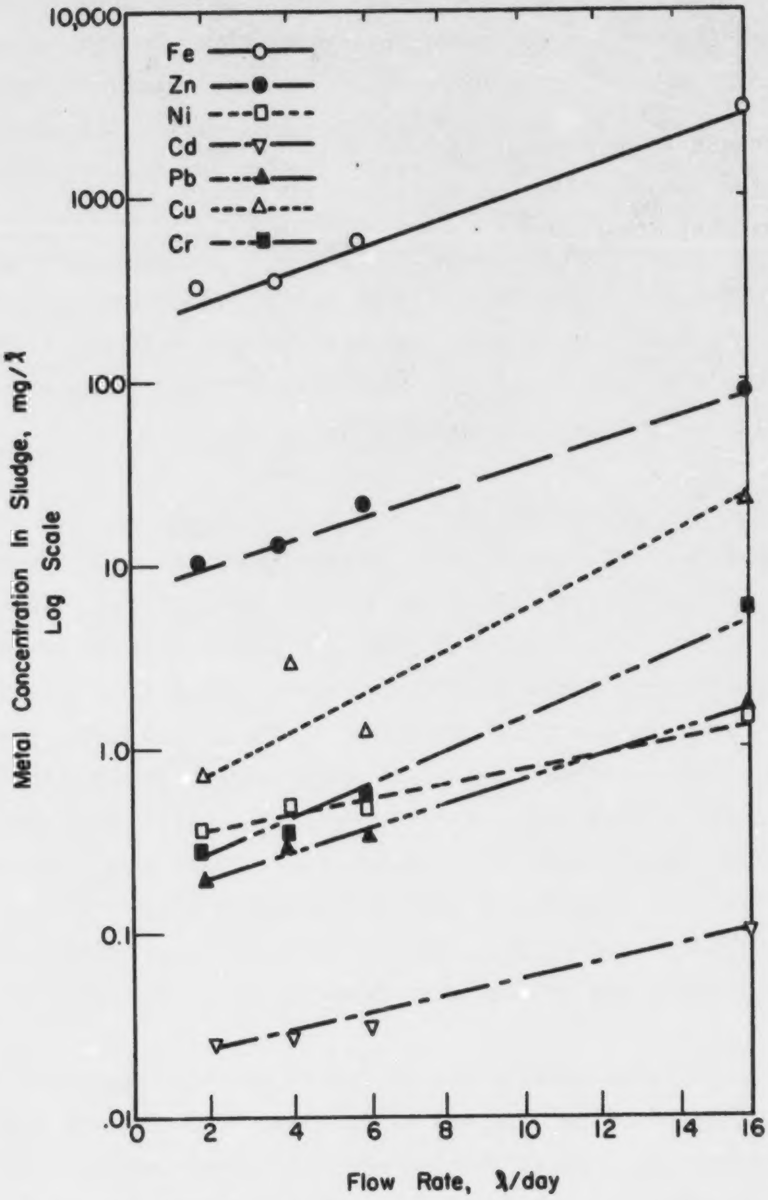

Figure 9. Effect of Increasing Hydraulic Loadings on the Metal Concentration in the Sludge Collected from the Bottom of the Anaerobic Filter

The COD:P ratio of 4360:1 should therefore be considered as an upper limit. The COD:N ratio of the feed was 39:1 indicating that no nitrogen limitation would occur. When the phosphates were distinguished in total, soluble and orthophosphates, it was noted that about three fourths was present in the suspended solids form (Figure 7c). The total phosphate concentration, therefore parallels the suspended solids measurements, as observed during the evaluation of the third shockload. During the toxicity period a significant decrease was observed in total phosphate concentration, probably as a result of the formation of metal phosphate precipitates. After addition of 75 mg/ℓ Na_2S, higher soluble phosphate concentrations were observed, possibly because less metals were available to form precipitates with the phosphates; the total effluent P concentration, however, did not change substantially.

Factors Affecting Effluent Organic Matter Concentrations

It was noted that after addition of the sulfides, the differences between total COD and the COD in filtration of 0.45 μm Millipore filter became more substantial. As it was felt that the higher organic solids content could be due to insufficient settling within the unit, a solids collection compartment of 3.8 liter was added to the column below the influent inlet compartment (Figure 1). Visual observations showed that solids were collected in this compartment to gradually build up a sludge slurry. Comparison of the effluent data showed both a lower total COD and soluble COD in period 3 as compared to period 2 probably as a result of the solids collection device (Figure 5a). The differences in suspended solids concentration between the two periods, however, were not noticeable.

In order to determine whether the effluent concentration is solely determined by organic loading, and not by influent concentration and hydraulic detention time, the organic loading was maintained constant, while the influent concentration was doubled, by feeding the unit with undiluted leachate instead of the 1:2 diluted leachate. Simultaneously the detention time was doubled to maintain the constant loading. The results in Figure 5, 6 and 7 indicate a temporary deteriorating effluent quality of

COD, fatty acids and carbohydrates. Both pH and bicarbonate alkalinity decreased during this period but returned to initial values after a 15-day period. After this initial adaption, effluent qualities were generally similar for period 3 and 4, indicating that the influent concentration does not affect the effluent quality under the conditions studied; however, it does affect the percentage of COD removal. Similar conclusion was reached by Young and McCarty (1968, 1969). They noted that when the organic loading was maintained while both the influent concentration and the hydraulic detention time were decreased, the unit gave a constant percentage COD removal at low loadings but a decreasing percentage at high loadings. Jennett and Dennis (1975) found that at a constant removal rate of 3.5 kg COD/m^3 day (220 lb COD/1000 cu ft day) the percentage removal decreased from 98 percent to 95 percent and 94 percent respectively, when the influent concentration decreased from 16,000 mg/ℓ, 8000 mg/ℓ and 4000 mg/ℓ. Contrary to the results in the present study, they also noted that the actual effluent concentration decreased. Based on these results one would conclude that recirculation does not affect the effluent quality as the latter is only determined by the substrate removal rate. Recirculation, however, is necessary to maintain sufficient high pH values to treat the acidic feed. A completely mixed regime would allow utilization of the entire length of the column for substrate removal; in plug flow units, however, only the lower one meter (3.3 ft) is effective (Young and McCarty 1968, 1969; Jennett and Dennis, 1975). As such, increasing the height of the completely mixed unit with respect to the area at the base will reduce the total column requirement for the same degree of treatment and, therefore, lower construction costs (Germain, 1964).

Effect of Removal Rate on Organic Matter

Since the effluent organic matter concentration is mainly determined by the substrate removal rate of the unit and not by influent concentration or hydraulic detention time, the third phase of the study was conducted to establish such relationships. During the initial 30 days of the third phase, the detention time was similar to the fourth period of the second phase, i.e. 74 days. Although slightly less than one volume turn-over was realized, analysis of the effluent quality indicated that steady state operations were realized (Figure 10 and 11).

When the detention time of the unit was reduced to 17.5 days, higher effluent concentrations were generally observed (Figure 10 and 11). An increase was observed for both the biodegradable fatty acids and for the less readily degradable carbohydrates and aromatic hydroxyls. Reduction of the detention time to 7.5 days caused a further increase in organic matter concentration in the effluent. As the quantity of available leachate was limited, only a 0.7 volume turnover was realized at this loading. The effluent parameters, with exception of the carbohydrates, however, indicated that steady-state operations were obtained. Both pH and inorganic carbon concentrations showed that the unit was effectively operating at this detention time. The phosphate analyses also indicate that this nutritional element is not limiting the biological growth at higher rates of substrate removal. Although a larger amount of organic matter is removed at the higher loading, the resulting higher organic matter content in the effluent is a major disadvantage. A material balance during Phase III indicated that 93 percent of the COD could be accounted for by the methane gas leaving the unit. The effluent concentration generally reached new equilibrium levels after about 2 days after a change in the loading. Young and McCarty (1968, 1969) similarly noted that when the loading to the anaerobic filter was increased, the gas production rate increased within two days. Jennett and Dennis (1975) found that immediately after a loading change the effluent COD concentration increased temporarily but returned to new steady-state levels after about 10 days. They also noted that the temporary increase in effluent COD was more noticeable when the loading increase resulted from a higher influent concentration than from a decrease in detention time. This tends to agree with the results obtained in this study.

Although the actual effluent concentration is determined by the rate of substrate removal, the percentage of removal, however, is determined by the hydraulic detention time. The removal percentage for the completely

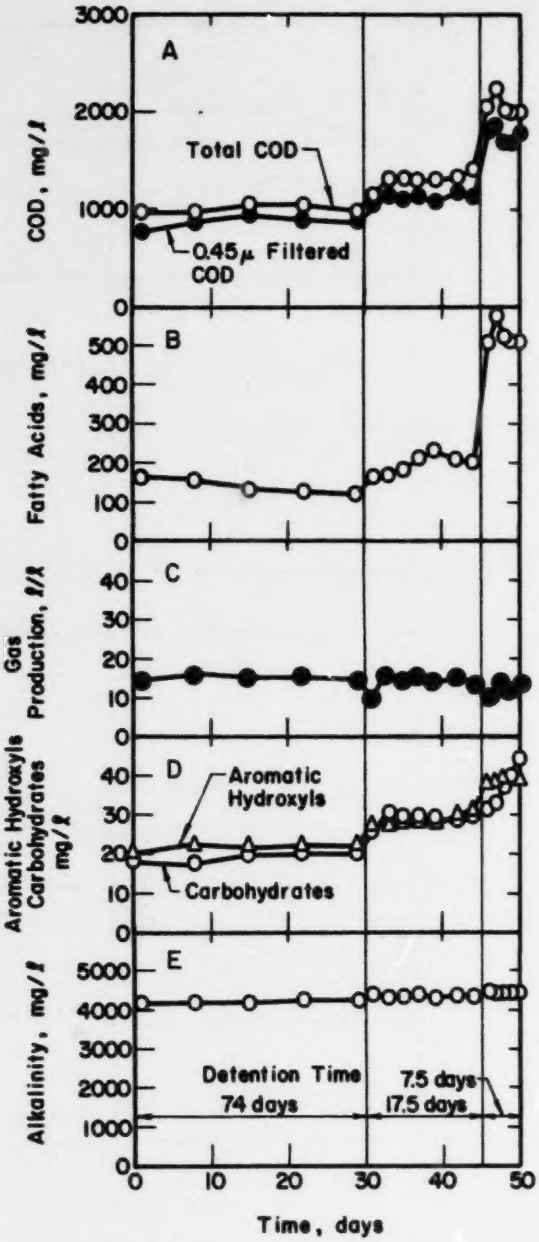

Figure 10. Effluent Quality During Phase III as Measured by COD, Fatty Acids, Gas Production, Carbohydrates, Aromatic Hydroxyls and Alkalinity

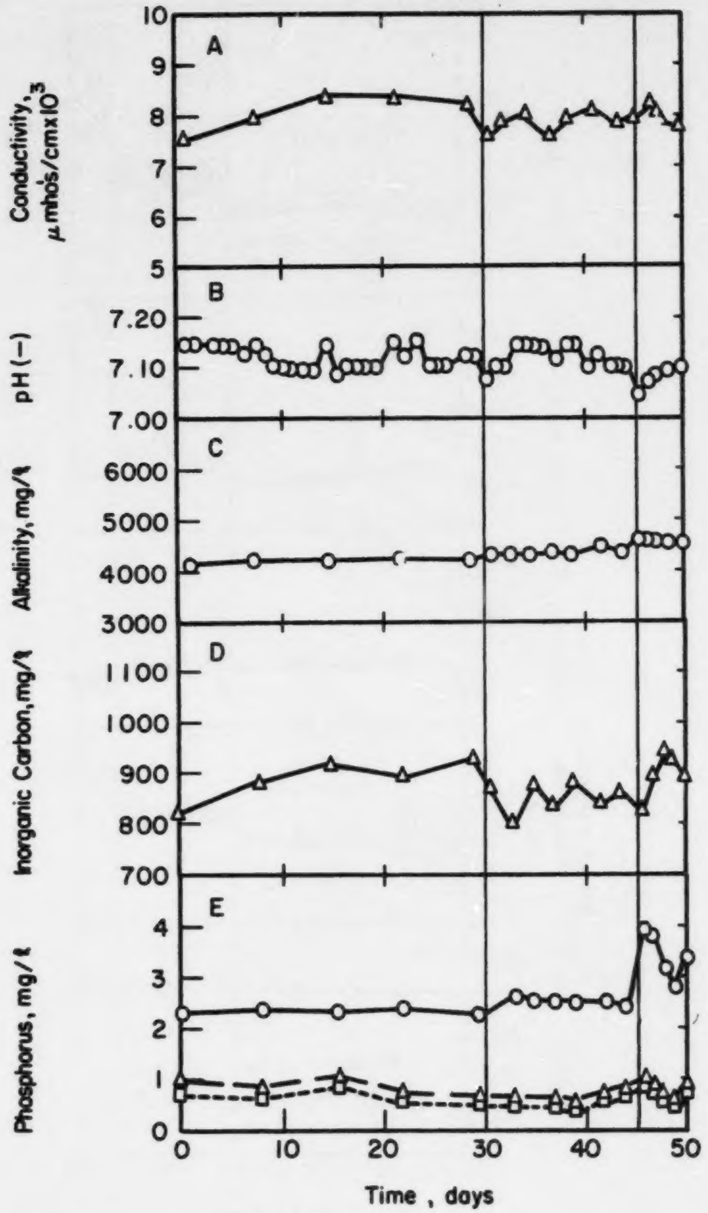

Figure 11. Effluent Quality During Phase III as Measured by Conductivity, pH, Alkalinity, Inorganic Carbon and Phosphorus

mixed unit was therefore calculated during the three detention times of 74, 17.5 and 7.4 days in Phase III and the 3 day detention time during the shockloading in Phase II (Figure 12). In addition, the percentage removal as predicted for plugflow units by Young and McCarty (1968, 1969) is shown for comparison. They formulate that the efficiency was inversely related to the hydraulic detention time. The results of the two systems indicate that at long and short detention times reasonable agreement is observed. At intermediate ranges, however, the observed results showed higher percentages of removal for the unit in the present study. The data also indicate that the unit should be operated above a detention time of 7 days in order to obtain more than 95 percent COD removal.

At the end of the third phase, tap water was introduced in the unit to study whether the mixing regime as a result of the recirculation agreed with the completely mixed model. The results of the color dilute-out clearly indicate that this is still true after accumulation of appreciable amount of biomass, since 63.2 percent is removed after one volume turnover (Figure 13a). The initial section of the total P curve (Figure 13b) shows an identical result, but shows higher removals after about one volume turnover, possibly as a result of precipitation under the more aerobic conditions resulting from the tap water additions. The suspended solids show the highest decrease since their removal is also aided by sedimentation. A lower dilute-out is observed after about 70 percent of the suspended solids are removed indicating that the remaining fraction consists of smaller particles.

Effluent Organic Matter Composition

An evaluation of the relative compositions of the effluent organic matter at the three loadings is shown in Figure 14. The fourth data point was obtained during Phase I when the unit was subject to a shockload in which the retention time was reduced to three days for a two day duration. The results in Figure 14 show that with increasing loadings a larger percentage of the organic matter consisted of free volatile fatty acids (Figure 14)

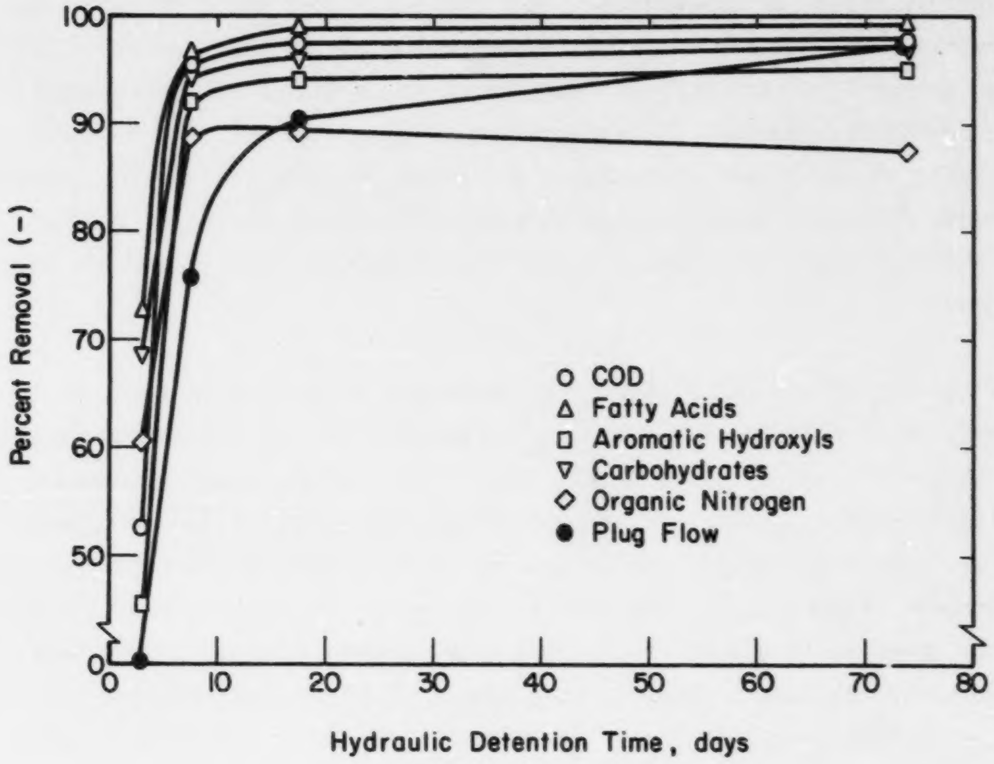

Figure 12. Percentage Organic Matter Removal at Different Detention Times

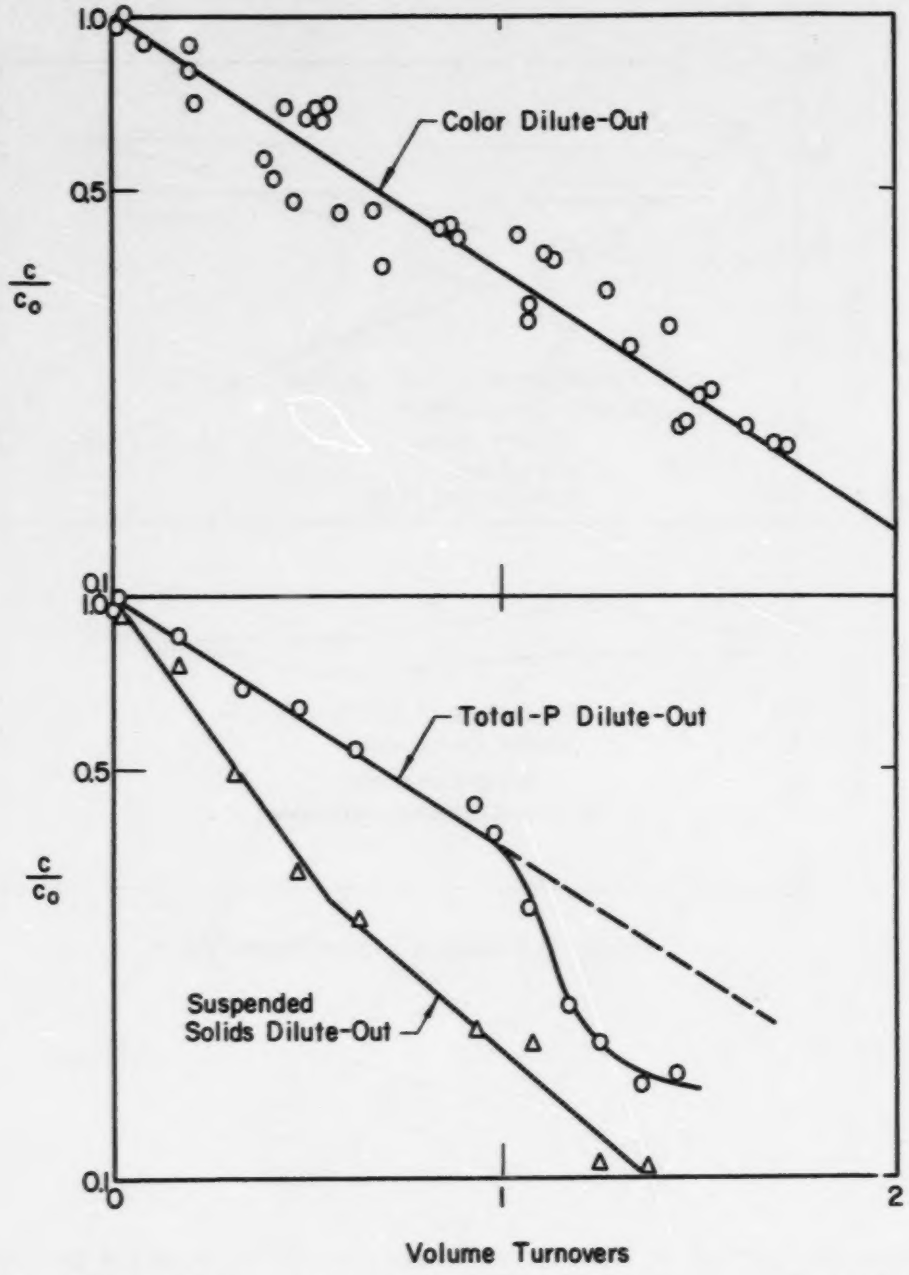

Figure 13. Dilute-Out Curves for Color, Total Phosphorus and Suspended Solids

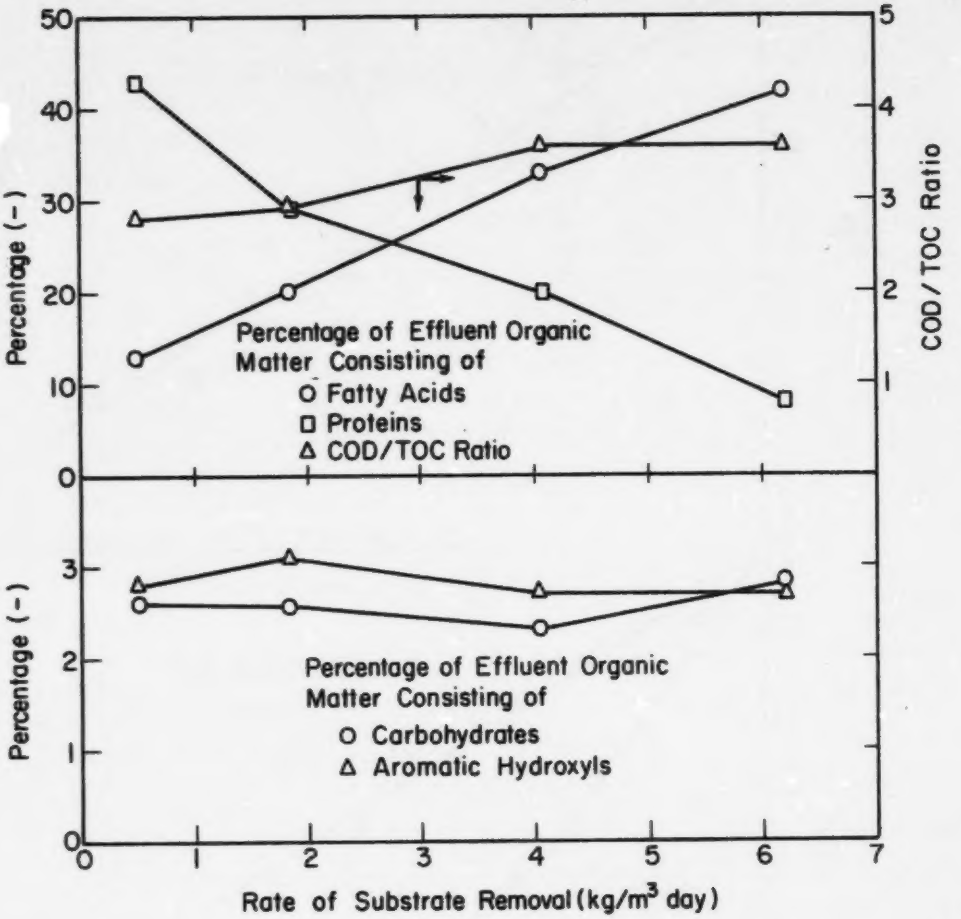

Figure 14. Effect of Rate of Substrate Removal on Relative Organic Matter Composition of the Effluent

assuming a COD/weight ratio of 1.07. This would indicate that the methane fermenting bacteria are determining the overall substrate removal rates. Young and McCarty (1968, 1969) also observed that at low loadings the percentage fatty acids decreased with decreasing loadings. However, at removal rates about 1.5 kg COD/m^3 day (94 lb COD/1000 cu ft day) the percentage fatty acids decreased with increasing removal rates, possibly indicating that at this rate the acid fermenting bacteria also become limiting. A similar optimum at 1 kg COD/m^3·day (63 lb COD/1000 cu ft day) was obtained with data from Jennett and Dennis (1975); Plummer *et al.* (1968) also observed a decreasing percentage fatty acids with increasing removal rates above a removal rate of 1.5 kg/m^3·day. A lower optimum was of 0.2 kg COD/m^3 day was calculated from data of Arora *et al.* (1975). This lower optimum may have been due to the less degradable nature of the substrate as reflected by the low BOD/COD of 0.52. The data, however, indicate that the above mentioned optimum corresponds to a substrate removal rate between 1 and 1.5 kg COD/m^3·day. The absence of such optimum in the present study is due to the fact that fatty acids are already present in the influent stream. The decrease of the percentage fatty acids at decreasing removal rates is reflected by a decrease of the COD/TOC ratio's in the effluent, indicating an increase of the oxidation state of the organic (Figure 14a).

The trend observed for the fatty acids is opposite that of the nitrogenous organics assuming a COD/N ratio of 10. The highest actual concentration was obtained at the high loading, which decreased at the intermediate loading and showed a slight increase at low loadings; the soluble COD showed a continuous decrease resulting in a gradual increasing percentage nitrogenous organics. This trend is in agreement with studies by Chian and DeWalle (1975) who noted an increase in amino acids and nitrogenous organics after removal of the free volatile fatty acids using an aerobic system. The data in Figure 14a would indicate that a similar trend is occurring in anaerobic systems. DeWalle and Chian (1974) noted a substantial increase of high molecular weight carbohydrates after removal of both fatty acids and amino acids. The absence of such increase in the present study (Figure 14b) is probably due to the low bacterial growth rates which are characteristic of anaerobic systems. This was confirmed in further tests in which the effluent of the anaerobic filter was subsequently treated in an aerated lagoon; after the fatty acids were removed a substantial increase in high molecular weight carbohydrates was observed.

Sludge Production

A solids balance was made during the third phase of the study. For this purpose any solids accummulated in the bottom section were removed prior to Phase III. At the end of the fifty-day period, sufficient solids were accummulated in the bottom section. A total of 2.5 liters of sludge were removed. The sludge had a density of 1.026 g/cm^3 and contained 3.86 percent solids with a volatile solids/total solids ratio of 0.377 to give a total of 37.3 g volatile solids. The solids density in the present study is less than observed by Arora *et al.* (1975) who obtained an 8 percent slurry with a volatile solids/total solids ratio of 0.34, but more than the 2.3 percent observed by Jennett and Dennis (1975). The calculated average concentration of volatile suspended solids in the effluent samples was 106 mg/ℓ. As 20 mg/ℓ was present in the influent the net accummulation of suspended solids during the fifty-day period was 11.2 g. Thus, about 67 percent of the recoverable solids generated in the unit will accumulate in the bottom section and can be removed by subsequent discharge to sludge drying beds; 33 percent of the recoverable solids were present in the effluent of the unit. During the fifty-day period a total of 3992 g of COD was removed, resulting in an apparent net synthesis of 0.012 g VSS formed/g COD removed. A higher yield would have been obtained if the accumulation of biological solids onto the plastic media slabs had been measured. The present value compares favorably with data calculated by Young and McCarty (1968, 1969) who observed a net synthesis of 0.015 g VSS/g COD for fatty acid waste and 0.118 g VSS/g COD for a protein-carbohydrate mixture. Jennett and Dennis (1975) using a pharmaceutical waste consisting mainly of methanol, observed a yield of 0.027 g VSS/g COD. The former included in their calculation the solids that were attached to the filter media, while the latter measured the solids that were loosely attached to the media and could be removed through the sampling ports. Assuming a VSS/P in the synthesized sludge of 60:1 (McCarty and Speece, 1963), the maximum COD"P ratio in the feed should be 5000:1 based on an apparent net synthesis of 0.012 g VSS formed/g COD removed. This ratio is comparable to that actually measured in the influent stream.

Several factors have been recognized to determine the amount of solids leaving the anaerobic filter. Young and McCarty (1968, 1969), observed a gradual accumulation of solids in the anaerobic filter during which period the effluent suspended solids remained low. Only after the filter reached its maximum storage capacity would the effluent solids show an increase. More than 70 percent of the solids synthesized within the filter can be retained in the filter when treating a fatty acid waste. However, with substrates that result in higher yields such as protein-carbohydrate wastes only 30 percent may be retained (Young and McCarty, 1968, 1969). When the influent waste contains solids, no net removal may be observed (Jennett and Dennis, 1975). Both Plummer *et al.* (1968) and Jennett and Dennis (1975) observed that the solids concentration was mainly determined by the hydraulic detention times. The present data are in agreement with both studies (Figure 7b). In addition, it is noted that the porosity of the filter may have a large effect on the solids concentration which is to be expected since a lower void ratio will increase the collision frequency between the solids and the filter media. The suspended solids, for example, were only 10 mg/ℓ at a void ratio of 0.42 (Young and McCarty, 1968), 34 mg/ℓ at a void ratio of 0.47 (Jennett and Dennis, 1975), 40 mg/ℓ at a void ratio of 0.46 (Foree and Reid, 1973), 450 mg/ℓ at a void ratio of 0.85 (Mueller and Mancini, 1975), and 1200 mg/ℓ at a void ratio of 0.68 (Plummer *et al.*, 1968). The average suspended solids concentration of 190 mg/ℓ at a void ratio of 0.94 as observed in this study compares favorably with other data and is probably due to the detention times which were higher than most other studies.

Effect of pH on Gas Production

After termination of the Phase I, II and III studies, all the analytical data were correlated with each other. When the daily gas production rates were related to the effluent pH values, the results in Figure 15 indicate that the highest rates are observed at a pH of 7.1. The relatively low gas production rates at a pH of less than 6.9 were observed during the period of heavy metal toxicity. The rate of optimum pH values as observed in the present study is considerably smaller than other researchers have found (Figure 16). Speece and Clark (1969), for example, still obtained half of the optimum gas production rates at a pH value of as low as 5.4, using anaerobic filters fed with acetate. However, they related gas production to the average pH at different depths in the plug-flow unit and a more narrow band would have been obtained if the pH in the effluent had been used for such comparison.

Clark and Speece (1970) also summarized existing literature data relating gas production of anaerobic digesters to corresponding pH values, indicating that at a pH of 6.0 the gas production was reduced by 50 percent. Using laboratory digesters, Thiel *et al.* (1968) came to a similar conclusion. Heukelekian and Heinemann (1939) measured the viable anaerobic bacteria at different pH values and noted a more gradual decrease at decreasing pH values as compared with the other studies. Speece and Clark (1969) noted that the inhibition of the methane fermenting bacteria at low pH values was bacteriostatic rather than bactericidal and could be reversed after pH adjustment. The inhibition at low pH values was attributed to hydrogen ions and undissociated fatty acids, while the lower gas production at high pH was thought to be due to unionized ammonia. It also could result from substrate limitation as at high pH all the fatty acids are dissociated and therefore not available for substrate uptake. McCarty and McKinney (1961) reported that free ammonia becomes toxic at concentrations of 150 mg/ℓ. Since the high pH values in the present study generally occurred at low loadings, the low gas production at higher pH values is likely due to substrate limitation. The average NH_3-N concentration in the effluent was 540 mg/ℓ which value did not change considerably during the study period.

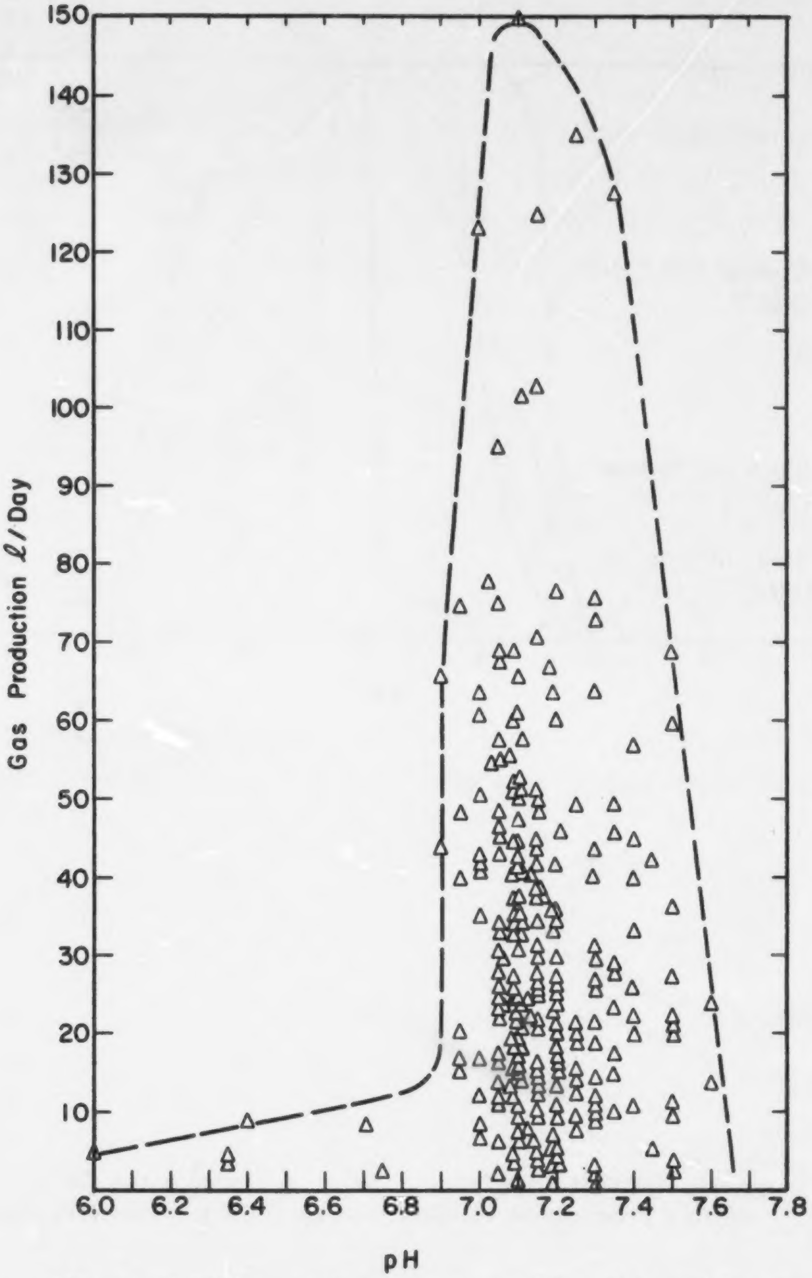

Figure 15. Effect of Effluent pH on Corresponding Rate of Gas Production

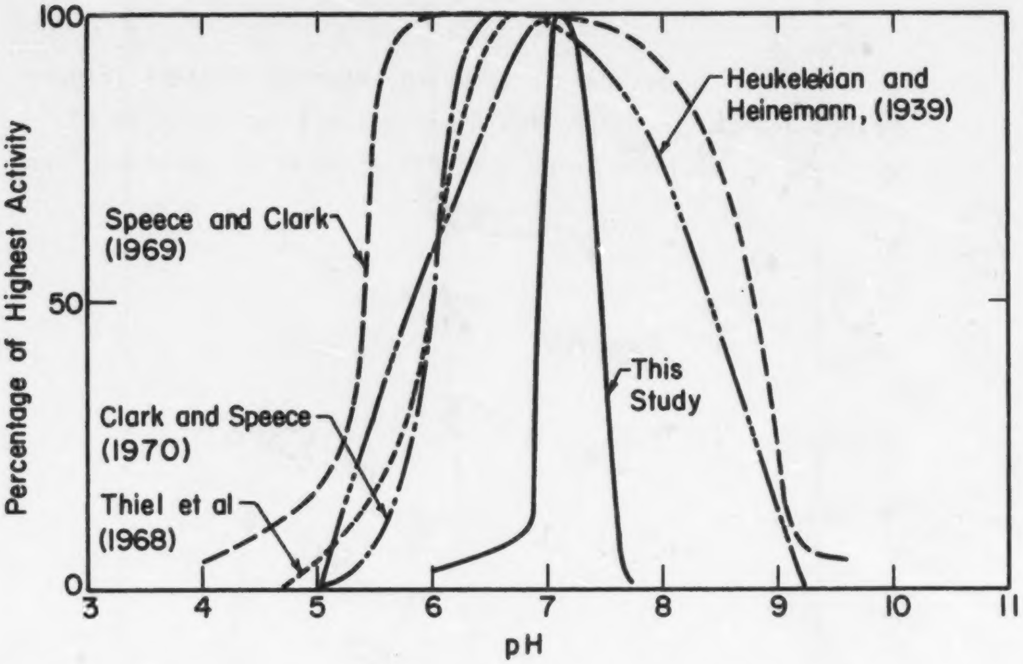

Figure 16. Effect of Effluent pH on Corresponding Relative Rate of Gas Production as Observed by Several Investigators

This would only correspond to about 10 mg/ℓ free ammonia at the pH of the effluent which is well below the stated toxic level.

Gas Composition

The gas composition measured in the present study was within the range of values reported by other investigators studying anaerobic filters (Figure 17). The methane content was generally 75 percent but decreased to 63 percent at the highest loading. Using a similar type of wastewater, Foree and Reid (1973) reported a 70 percent methane content. The decrease of the methane content at higher rates of substrate removal was also observed by Thiel *et al.* (1968) who noted that such a decrease corresponded to an increase in free volatile fatty acids and a decrease in pH. This also resulted in a higher CO_2 liberation and a lower bicarbonate alkalinity in solution. Speece and Clark (1969) similarly noted a 95 percent methane content at a pH of 8 which linearly decreased to 70 percent at pH 7, 50 percent at pH 6 and 30 percent at pH 5.

The amount of gas produced in the present study always corresponded closely to the amount of organic matter removed. During the three increasing loadings (Figure 10 and 11) the amount of methane gas corresponded respectively to 95 percent, 93 percent and 92 percent of the amount of COD removed. This is in close agreement with results obtained by Foree and Reid (1973) who recovered 99 percent using a similar waste stream. Using a fatty acid waste stream Young and McCarty (1968, 1969) recovered 100 percent, while Speece and Clark (1969) obtained 94 percent. A waste stream containing carbohydrates resulted in a recovery of 93 percent (Young and McCarty, 1968, 1969) 100 percent (Mueller and Mancini, 1975), more than 100 percent (Foree and Lovan, 1971). Jennett and Dennis (1975) on the other hand only accounted for 50 percent of the theoretical gas production at low loadings which, however, increased to 90 percent at higher loadings. El-Shafie and Bloodgood (1973) similarly only accounted 50 percent of theoretical gas production, while Caudill (1968) only observed 10 percent of the theoretical production. It was noted in the present study that the wet gasmeters did not register satisfactory at relatively low gas flow rates which may explain the results obtained by Jennett and Dennis (1975).

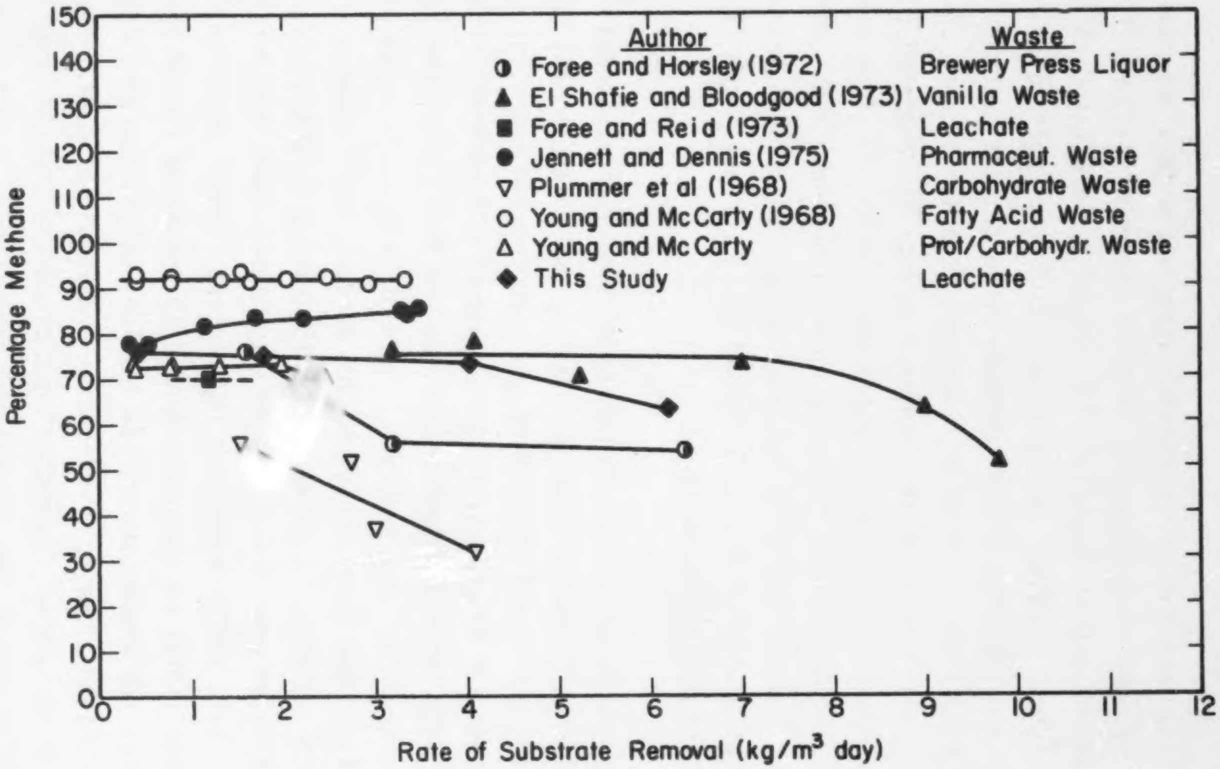

Figure 17. Effect of Rate of Substrate Removal on Gas Composition

Effluent Buffer Capacity

It was noted in the previous section that several factors influenced the pH and buffer capacity of the system. Figure 10 and 11 indicated that the alkalinity as determined by titration was relatively insensitive to changes in the bicarbonate concentration as measured with the inorganic carbon channel of the TOC analyzer. This is a result of the ionized fatty acids which register in the alkalinity determination, but are not very effective in maintaining the pH of the solution due to their low pK values. It was therefore not surprising to note a general decrease in the inflection point of the effluent titration curve and the fatty acid concentration in the effluent (Figure 18). This then shows that the alkalinity as determined by titration is not a useful monitoring tool to measure the buffer capacity of the system, and more useful information is obtained when both the pH, inorganic carbon and fatty acid concentrations are monitored.

Kinetics of Substrate Removal

The kinetic consideration discussed earlier indicate that at relatively low substrate concentrations the removal rate increases linearly with effluent concentration. A compilation of the different studies evaluating anaerobic filters indicate that this is indeed the case (Figure 19). The rate of substrate removal was calculated as kilograms of COD removed per m^3 empty column volume per day; while the effluent concentration was used as the corresponding substrate concentration.

Considerable spread in the results of the different studies is apparent (Figure 19), indicating that other factors such as specific surface area, biodegradability, temperatures and mixing regime also exert a significant influence. Figure 19 also indicates that several effluent concentrations have a finite value when the removal rate approaches zero. The highest such residual concentration was noted in the present study and extrapolation would indicate a valuesof about 850 mg/ℓ. Four other studies showed such residual concentration. Further evaluation indicated that its magnitude generally increased with increasing influent concentrations. Residual effluent and related influent concentrations reported by these studies

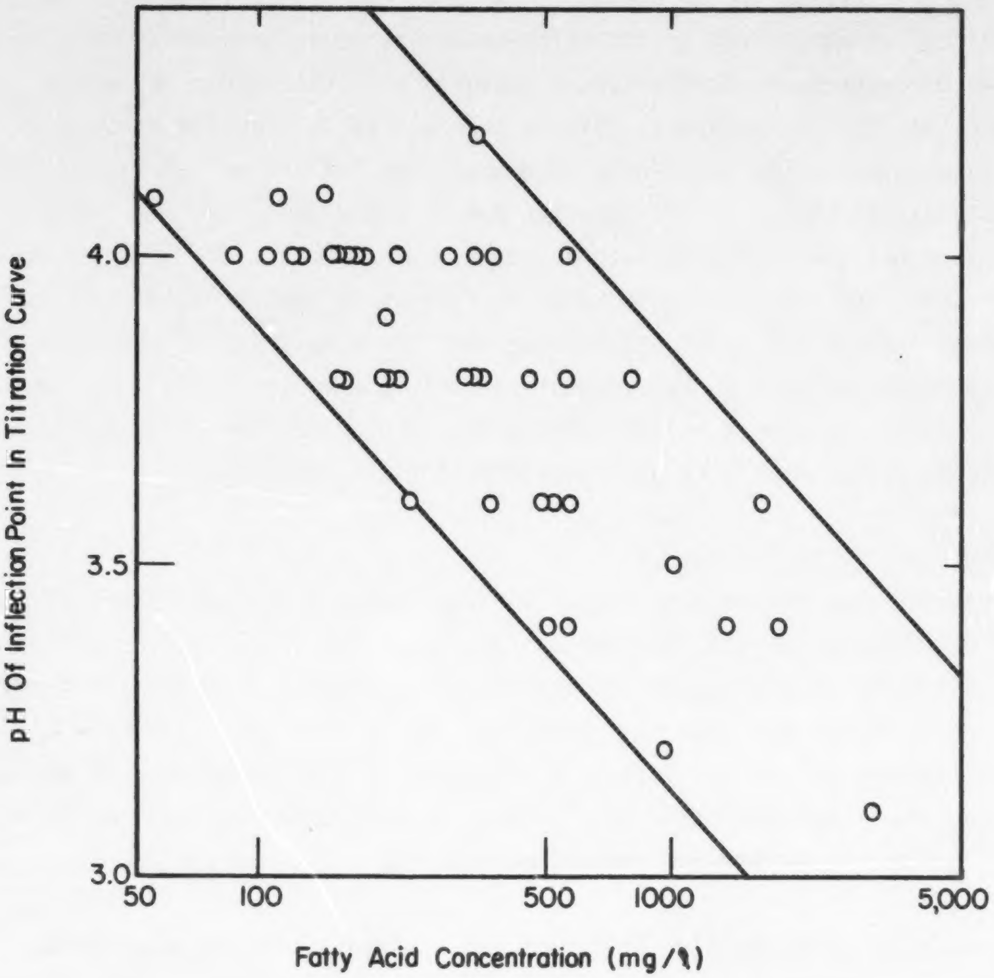

Figure 18. Relation Between pH of Inflection Point and Fatty Acid Concentration

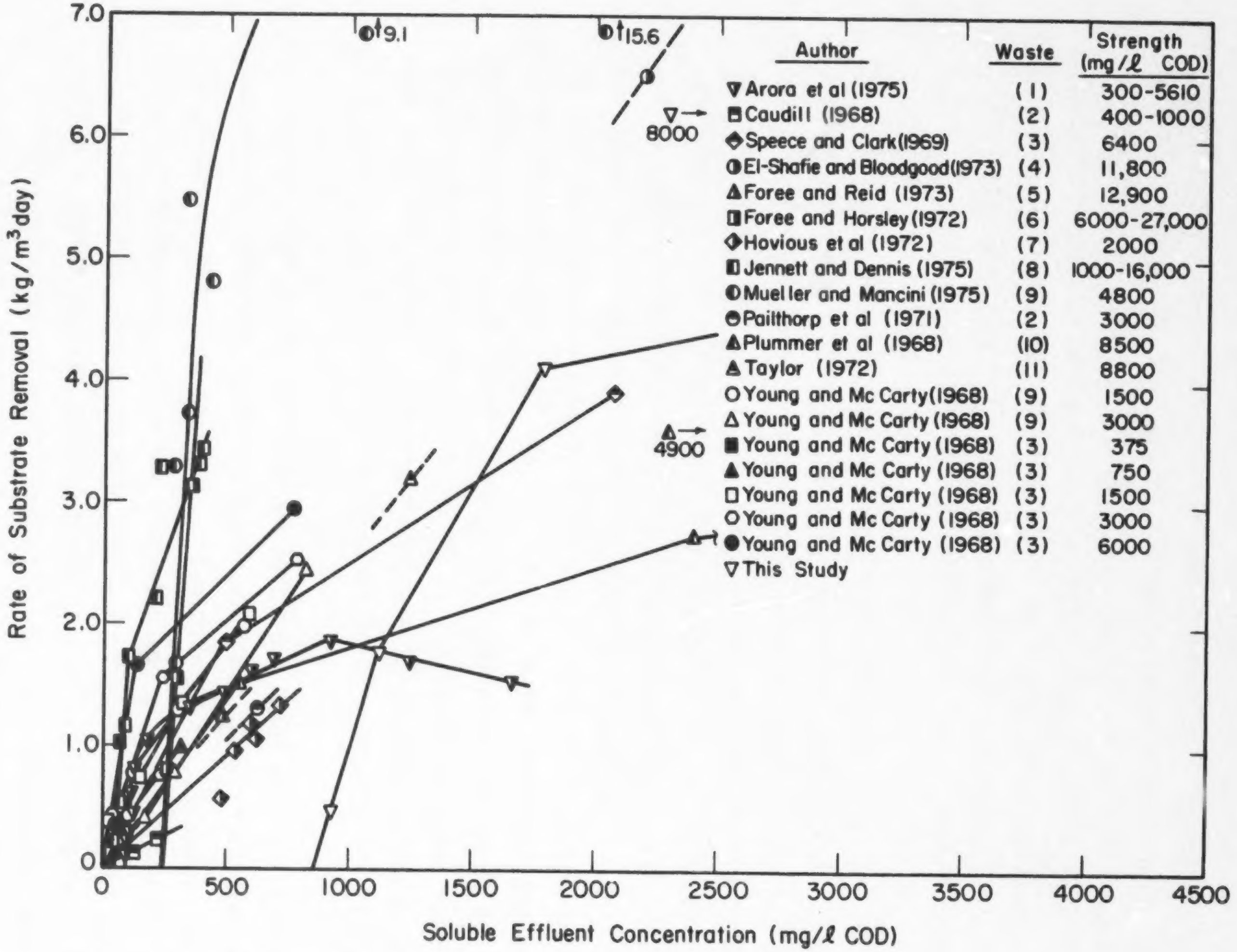

Figure 19. Effect of Substrate Removal Rate on Effluent Concentration as Measured in Different Studies using Various Wastes

were 850 mg/ℓ and 32,000 mg/ℓ (present study), 240 mg/ℓ and 13,000 mg/ℓ (Foree and Horsley, 1972), 230 mg/ℓ and 4,800 mg/ℓ (Mueller and Mancini, 1973), 100 mg/ℓ and 500 mg/ℓ (Arora *et al.*, 1975) and 50 mg/ℓ and 1,000 mg/ℓ, respectively (Jennett and Dennis, 1975). As higher influent concentrations correspond with a higher biomass present in the unit, the higher residual organics could also be the result of bacterially released organics or organics liberated during cell lysis. As a result of the presence of such residual concentrations, the slope of the relation between dF/V·dt and S_b (Equation 11) reached an almost infinite value; the k_2 (in Equation 11) values could therefore not be used for further analysis.

The data in Figure 19 also show that the substrate removal rates in only three studies approached a limiting value at high substrate concentrations. The result of one of these studies even showed a decreasing removal rate at such high concentrations indicating substrate inhibition (Arora *et al.*, 1975). According to Equation (8), a square root relationship would be obtained between the rate of substrate removal and substrate concentration at high concentrations. The data in the present study resulted in an exponent of 0.3 while the data of Plummer *et al.* (1968) gave a value of 0.4 which is less than the predicted value of 0.5. At veyr high concentration, dF/V·dt is expected to become independent of S_b as a result of which the value of the exponent decreases below 0.5 as observed in these two studies. This would indicate the validity of the model; however, insufficient data are as yet available to make a final conclusion.

A disadvantage of the model described by Equation (8) is that it does not define a maximum rate of substrate removal at high substrate concentrations. Such value, however, can be obtained by assuming that dF/V·dt and S_b follows a Monod hyperbolic relationship, whereafter the constants can be determined for a Lineweaver-Burk plot. When the reciprocal substrate removal is plotted versus that of the substrate concentration, a satisfactory linear relationship was not obtained. However, by using only the lowest values a maximum substrate removal rate of 7 kg COD/m^3 day and a half saturation concentration K_s of 1,500 mg/ℓ were calculated. The results of Plummer *et al.* (1968) gave values of 3.5 kg COD/m^3 day and 850 mg/ℓ respectively using three of the four reported data points. These maximum rates also tended to increase with biodegradability of the substrate and were 1.8 kg COD/m^3 day with a corresponding BOD/COD ratio of 0.52 (Arora *et al.*, 1975), 3.5 kg COD/m^3 day with a BOD/COD ratio of 0.61 (Plummer *et al.*, 1968) and 7 kg COD/m^3 day with a BOD/COD ratio of 0.65 (El-Shafie and Bloodgood, 1973). Of all studies, the highest rate was reported by Mueller and Manzini (1975) who observed a removal rate of 15.6 kg COD/m^3 day using a biodegradable dextrose-peptone mixture.

Specific Surface Area

Both Equation (8) and (11) indicate that the specific surface is the next most important factor determining the rate of substrate removal. When the $k_2 \cdot \frac{A}{V}$ values (in Equation 11) obtained by dividing the rate of substrate removal by the substrate concentration obtained at low substrate concentrations were related to the specific surface area in each reactor, no definitive correlation was observed (Figure 20). Excluded from Figure 20 were the data from those studies in which an increase in removal rate did not correspond to an increased substrate concentration as a result of which the k_2 values approached infinity. This was mainly due to the fact that none of the studies evaluated specific surface areas using the same substrate. Five studies, that evaluated the effect of specific surface areas using aerobic trickling filter, are included in Figure 20 and all show an increasing k_2 value as a result of the increasing surface area as predicted by Equation (11). The relation tends to be linear at low surface areas but becomes less than linear at high surface areas. This can be attributed to the bacterial growth which tends to fill up the void spaces as result of which the specific surface area at the liquid-biofilm interface becomes smaller than the specific surface area of the filter medium. Thus, although insufficient data are available from the different anaerobic filter studies, all results shown in Figure 20 tend to indicate that the value of k_2 would increase with increasing surface area. As synthetic media having large surface areas are several times more expensive than the rock media generally used, selection of the required specific surface area should be based on economic considerations.

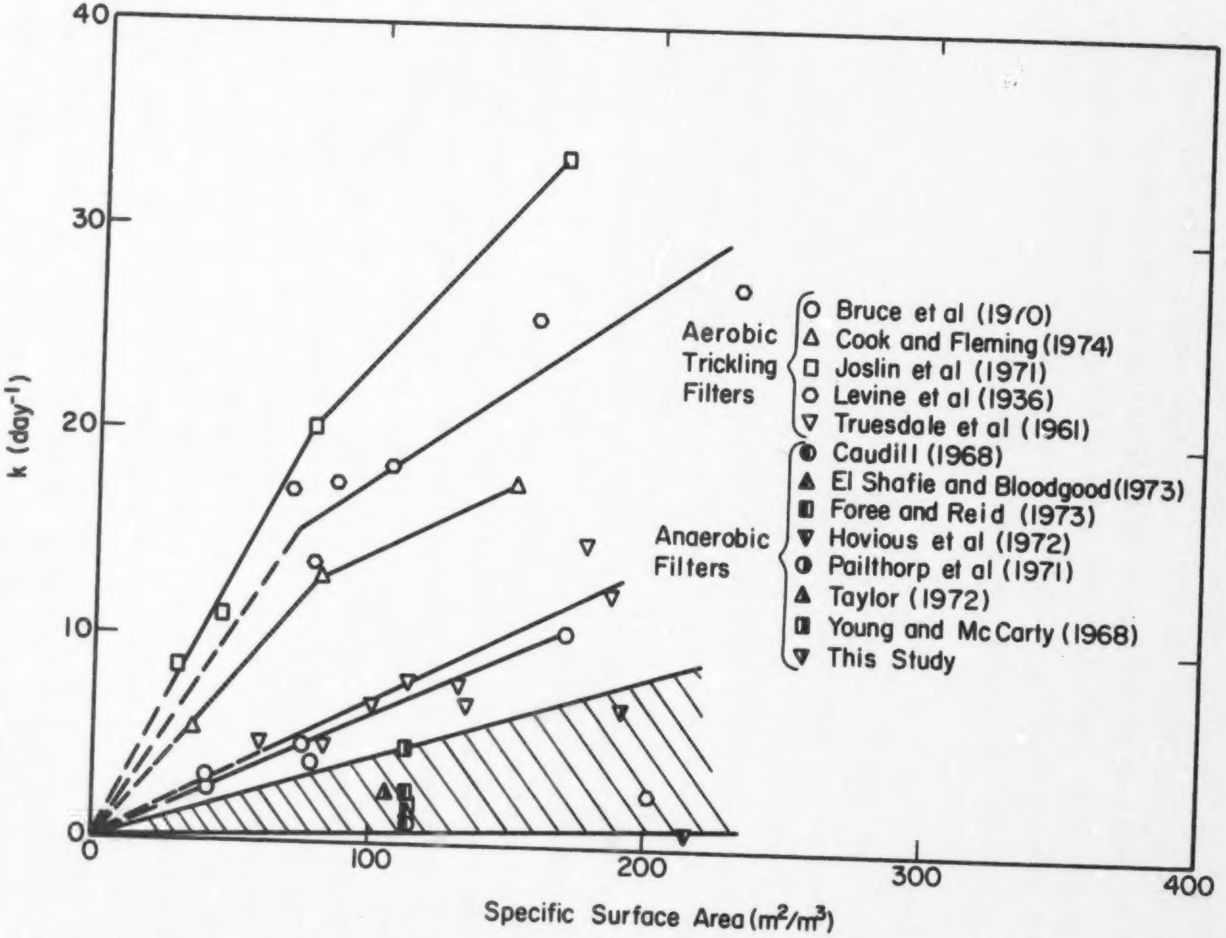

Figure 20. Effect of Specific Surface Area on Substrate Removal Coefficient

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Temperature

The effect of temperature on rate of substrate removal was evaluated in only two studies. Tadman (1973) using an industrial waste and column filled with Intalox saddles observed a 10 percent increase in removal efficiency when the temperature was increased from 25°C to 35°C. Caudill (1968) noted a 27 percent improvement in effluent quality when the temperature of an anaerobic filter unit treating a dilute fatty acid solution was increased from 26°C to 37°C. A preliminary comparison of heating costs versus the cost associated with increasing the specific area in the column by installing more expensive high surface area synthetic filter medium would indicate that the latter alternative is less costly in order to reach a desired treatment efficiency.

Mass Transfer

The effect of the flow velocity on the mass transfer in anaerobic filters as illustrated in Equations (11) (12) and (13) is difficult to evaluate. The most accurate data to illustrate this effect were obtained from the study by Young and McCarty (1968, 1969) when for a given flow rate in the column the substrate removal rate in each 30 cm segment was calculated and related to the concentration leaving that segment. Such calculations resulted to the concentration leaving that segment. Such calculations resulted in relations similar to those shown in Figure 19. The calculathe $k_2 \frac{A}{V}$ values showed a linear increase with actual flow rates within the column when plotted on log-log paper. From the limited data an exponent of 0.46 was calculated at flow velocities ranging from 1 to 10 m/d, which approaches the value of 0.5 predicted by Takeshi *et al.* (1972). Since the value of k_2 is related to K_L, this in turn indicates that it is beneficial for a given column volume to minimize the diameter whil maximizing the height of the column in order to obtain higher velocities and thus higher Reynolds numbers within the column.

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II

PHYSICAL CHEMICAL TREATMENT OF LEACHATE AND ANAEROBIC FILTER EFFLUENT

CONCLUSIONS

It was concluded that high-strength leachates cannot be effectively treated by physical-chemical treatment methods such as activated carbon adsorption, chemical precipitation and chemical oxidation. Activated carbon was observed to have a relatively low sorptive capacity when used to treat high-strength leachates. Although free volatile fatty acids, major constituents of such leachates, have a relatively low sorptive capacity, even lower capacities were noted for the non-fatty-acid fraction in leachate using activated carbon adsorption isotherms. Although an initial removal rate as high as 72% was obtained in activated carbon columns through which the diluted leachate was passed, much lower removal percentages were observed after passage of several bed volumes, and almost complete breakthrough occurred after 200 bed volumes. The column studies also illustrated the lower removal rate for the non-fatty-acid fraction in leachate. Activated carbon treatment of leachate is also unfeasible because headloss builds up rapidly in the column with the formation of iron precipitates. Although most of these precipitates were removed in the first backwash, difficulty was again encountered in subsequent runs.

Substantially higher adsorptive capacities of activated carbon were found for biologically pretreated leachate. Removal of biodegradable organics with an anaerobic filter increased the adsorptive capacity by 50%. Aerated lagoon treatment of the anaerobic filter effluent further removed low-mlecular-weight organics, resulting in an adsorption capacity of 0.174mg TOC/mg AC, a value approximately 2.5 times that observed for untreted leachate. Batch sorption tests showed that color and aromatic hydroyls are removed at lower carbon dosages than are high-molecular-weight carbohydrate-like materials. Membrane fractionation of the anaerobic filter effluent followed by activated carbon column treatment of each fraction showed relatively low removal rates for both the high-molecular-weight organics collected in the 18,000 MW UF retentate and the low-molecular-weight organics present in the 150 MW RO permeate. The highest removal rates were observed for fulvic-like organics of intermediate molecular weight. The increase in removal rates of organics in anaerobic filter effluent treated by aerated lagoon as mentioned previously was attributed to the higher adsorption characteristic of the low-molecular-weight organics.

Organic matter removal by lime precipitation, both before and after aeration, produced removal rates as low as 20 to 25%, and this removal was obtained at excessively large dosages. Other physical-chemical methods tested, such as ozonation and chlorination, resulted in similarly low organic matter removal rates. These results clearly show that physical-chemical treatment methods are not feasible for high-strength leachates and that extensive biological pretreatment is required. Of all physical-chemical methods tested, activated carbon treatment produced the highest organic matter removal rates.

INTRODUCTION

Solid waste leachate generated as a result of infiltrating rainwater contains high concentrations of organic matter. These substances can be removed by physical-chemical or biological treatment processes. After analyzing leachate samples from landfills of different ages, Chian and DeWalle (1975) noted a change in organic matter composition with increasing age of the fill: the percentage of free volatile fatty acids decreased, while the amount of refractory fulvic-like organics increased with age. Since free volatile fatty acids, di- and tricarboxylic acids and alcohols are degradable by aerobic and anaerobic bacteria, it was recommended that aerated lagoons and anaerobic filters be employed to remove organics from landfills which have generated leachate only recently. Physical-chemical methods such as lime coagulation, activated carbon adsorption and ozonation are generally less effective in removing such organics. Refractory organics generally formed by bacterial or chemical processes after removal of the degradable substrate, on the other hand, are more amenable to removal by physical-chemical processes then by bacterial processes.

The above recommendations have been borne out by several studies on the treatability of leachate. While Boyle and Ham (1974) noted a 93% COD removal in anaerobic digestors, Ho _et al_. (1974), using a similar leachate, obtained only a 34% COD removal rate using activated carbon at a maximum dosage of 20,000 mg/l. In subsequent column studies with granular Filtrasorb 400, maximum COD removal rates of up to 59% were observed at detention times greater than 20 minutes, based on analysis of the filtered second bed volume of leachate passed through the column. A pH reduction of the leachate to reduce the ionization of the dissociated free volatile fatty acids and to enhance their adsorption did not result in increased COD removal; in fact,the opposite was observed, with high COD removals corresponding to high pH. A similar comparison showed that anaerobic digestors were able to remove 99% of the leachate COD, while activated carbon at a dosage of 160,000 mg/l removed only 60%. The leachate studied was generated from a relatively recent fill, and 65% of the 2000 mg/l of TOC consisted of free volatile fatty acids. The study further noted that the non-fatty-acid fraction of the organic matter was adsorbed preferentially to the fatty-acid fraction. After biological treatment of a similar leachate, Pohland and Kang (1975) obtained removal rates as high as 91%, indicating that biological treatment followed by carbon adsorption will result in high organic matter removal rates. Cook and Foree (1974) obtained 68% COD removal in the first effluent bed volume when leachate was passed through an activated carbon column. Lime coagulation prior to the activated carbon treatment increased the overall COD removal to 81%. Van Flect et al. (1974) observed a 71% COD removal in the first effluent bed volume when leachate was passed through an activated carbon column. Aluminum pretreatment resulted in an overall COD removal rate of 94%. The highest COD removal percentage, 85%, was observed by Roy Weston Inc. (1974) at a carbon dosage of 10,000 mg/l. Because the leachate was obtained from an old abandoned fill which had undergone considerable biological stabilization, high adsorptive removals were to be expected.

These previous studies show that variable organic matter removal rates can be obtained in landfill leachate using activated carbon, a fact which may well reflect the variable nature of the organics. While activated carbon treatment of concentrated leachate from recently generating fills was not very effective, higher removal rates were obtained with leachate from more stabilized fills. High removal rates can perhaps be obtained with a combination of coagulation and adsorption or of biological pretreatment and adsorption. Chemical precipitation or chemical oxidation alone were not found to be very effective (Chian and DeWalle, 1976).

The purpose of the present study was to evaluate in greater detail the effect of organic matter composition on adsorptive behavior using leachate samples from different landfills, employing both adsorption isotherm tests and column studies. The effect of biological pretreatment using an anaerobic filter, with or without further aerobic effluent stablization, on activated carbon adsorption was studies more extensively, since preliminary work showed that this treatment sequence resulted in low organic matter concentrations.

MATERIALS AND METHODS

Batch adsorption tests were conducted with both undiluted and diluted leachate samples to which increasing dosages of activated carbon were added. The tests were conducted with Filtrasorb 400 (Calgon, Pittsburgh, PA) added to rectangular 250 ml precipitation bottles filled with 100 ml of the sample. Prior to adsorption, the leachate samples were filtered through a 0.45 μm Millipore membrane filter (Millipore, Bedford, MA) to remove the small amount of suspended solids initially present, since only the adsorption of soluble organics was to be evaluated in this study. After the carbon was added, the samples were shaken for 24 hours at 180 rpm. Distilled deionized water blanks to which activated carbon was added were included to correct for the small amount of organic compounds that dissolve from the carbon. The column studies were conducted with columns 15 cm and 30 cm long having empty bed detention times of 1.5 and 3.0 minutes, respectively, at a flowrate of 10 cm/min (2.5 gpm/ft^2) maintained by means of an accurate FMI positive displacement metering pump (FMI, Oyster Bay, NY). The columns were backwashed at a rate of 24 cm/min (6.0 gpm/ft^2) when the headloss buildup exceeded 200 cm. The leachate used for the carbon tests was obtained from a lysimeter filled with milled solid waste to which simulated rainfall was added (Chian and DeWalle, 1976).

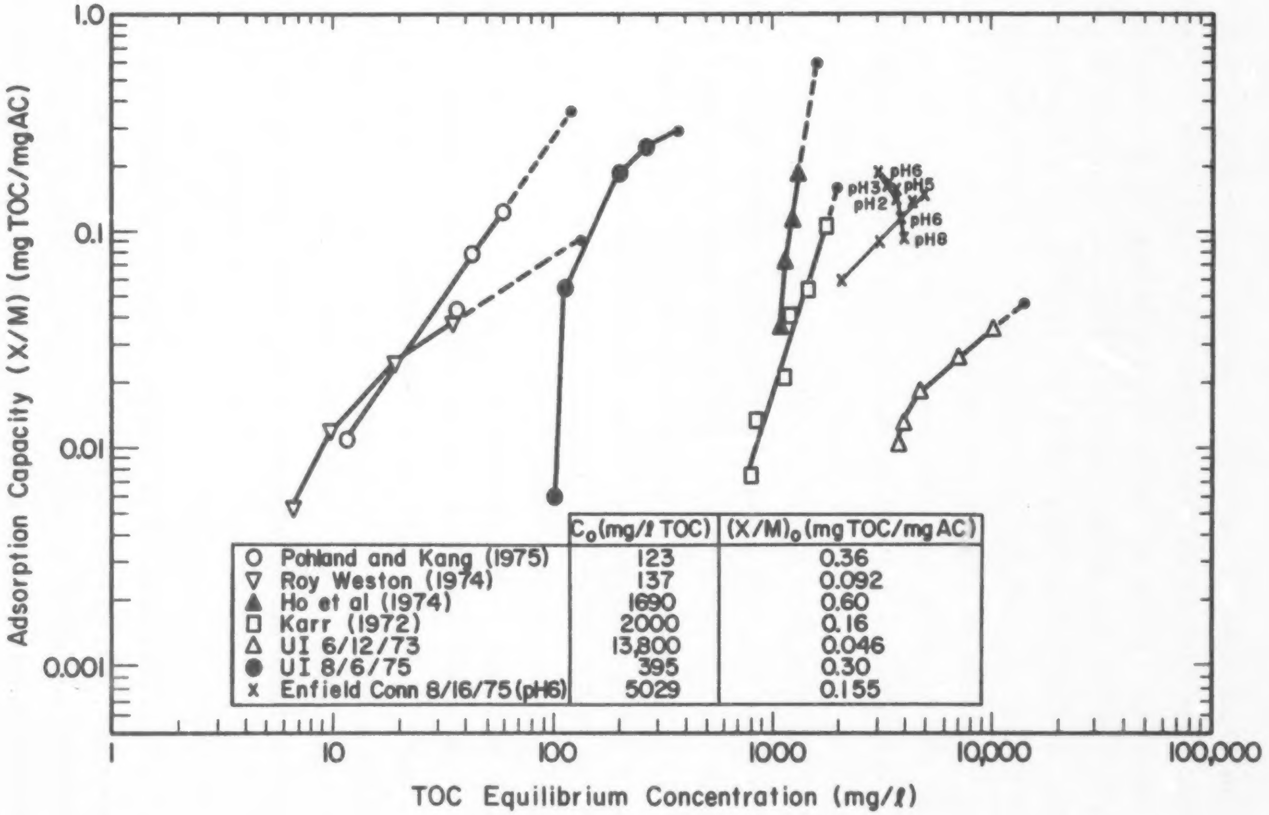
Anaerobic biological pretreatment of the leachate was accomplished with the unit described in Chapter I. Further aerobic degradation was conducted in a 80-liter batch reactor. Before and after aeration the soluble organic matter was characterized by molecular weight and major classes of organics using colorimetric tests. The molecular weight distribution was estimated using Sephadex G-25 and G-75 columns (Pharmacia, Piscataway, NJ). Larger quantities of the various molecular-weight fractions were obtained with a preparative ultrafiltration unit HFA-180 (Abcor, Cambridge, MA) followed by concentration of the UF permeate with a reverse-osmosis B-10 Permeator (DuPont, Wilmington, DE).

Each fraction was passed through an activated carbon column. Batch coagulation studies were conducted using a 1-liter sample to which a lime slurry was added. Following addition of the slurry, the content was rapidly mixed at 100 rpm for 1 minutes followed by slow mixing for 20 minutes at 25 rpm. The liquid was then settled for 30 minutes. The various parameters were measured in the decanted supernatant.

RESULTS AND DISCUSSION

Initially, the adsorption of the organic matter in the concentrated leachate was evaluated. The results of these tests (Figure 21) show a relative low adsorptive capacity: 0.045 mg TOC/mg AC, corresponding to a maximum COD removal rate of 73% at the highest dosage. When the leachate obtained from the same lysimeter two years later was tested, its concentration had decreased to 29% of the initial concentration. Its adsorptive capacity, however, was 6.5 times as high, possibly indicating that gradual biological stabilization of the solid waste and of the interstitial leachate resulted in organics more amenable to physical adsorption. This explanation is also indicated by the results in Figure 21 since a higher maximum adsorptive capacity tends to be associated with a lower initial organic matter concentration. The positive effect of biological stabilization is further examplified by the results of Karr (1972), who noted a maximum adsorptive capacity of 0.16 mg TOC/mg AC using leachate without any biological treatment. Using a similar wastestream after aerobic biological treatment, Pohland and Kay (1975) obtained a capacity of 0.36 mg TOC/mg AC a factor of 2.3 higher. Since the free volatile fatty acids are dissociated at the pH of the leachate, higher adsorptive capacities are to be expected at decreasing pH values when these acids are no longer ionized. The results in Figure 21 indeed show the highest capacity at a pH of 4. The lowest adsorptive capacity was observed at a pH of 8. These results are contrary to those of Ho _et_ _al_. (1974), who did not note any pH effect, quite possibly because of the absence of any fatty acids in the analyzed sample.

Since higher adsorptive capacities tended to be associated with lower initial concentrations, several adsorption tests were made at the lowest initial concentration noted in Figure 21; i.e., 120 mg/l TOC. Using the diluted leachate dated 6/12/73, a maximum adsorptive capacity of 0.068 mg TOC/mg AC was obtained (Figure 22), 1.48 times higher than the capacity



	C_o(mg/ℓ TOC)	$(X/M)_o$ (mg TOC/mg AC)
○ Pohland and Kang (1975)	123	0.36
▽ Roy Weston (1974)	137	0.092
▲ Ho et al (1974)	1690	0.60
□ Karr (1972)	2000	0.16
△ UI 6/12/73	13,800	0.046
● UI 8/6/75	395	0.30
x Enfield Conn 8/16/75 (pH6)	5029	0.155

Figure 21. Activated Carbon Adsorption Isotherms with Different Leachate Samples

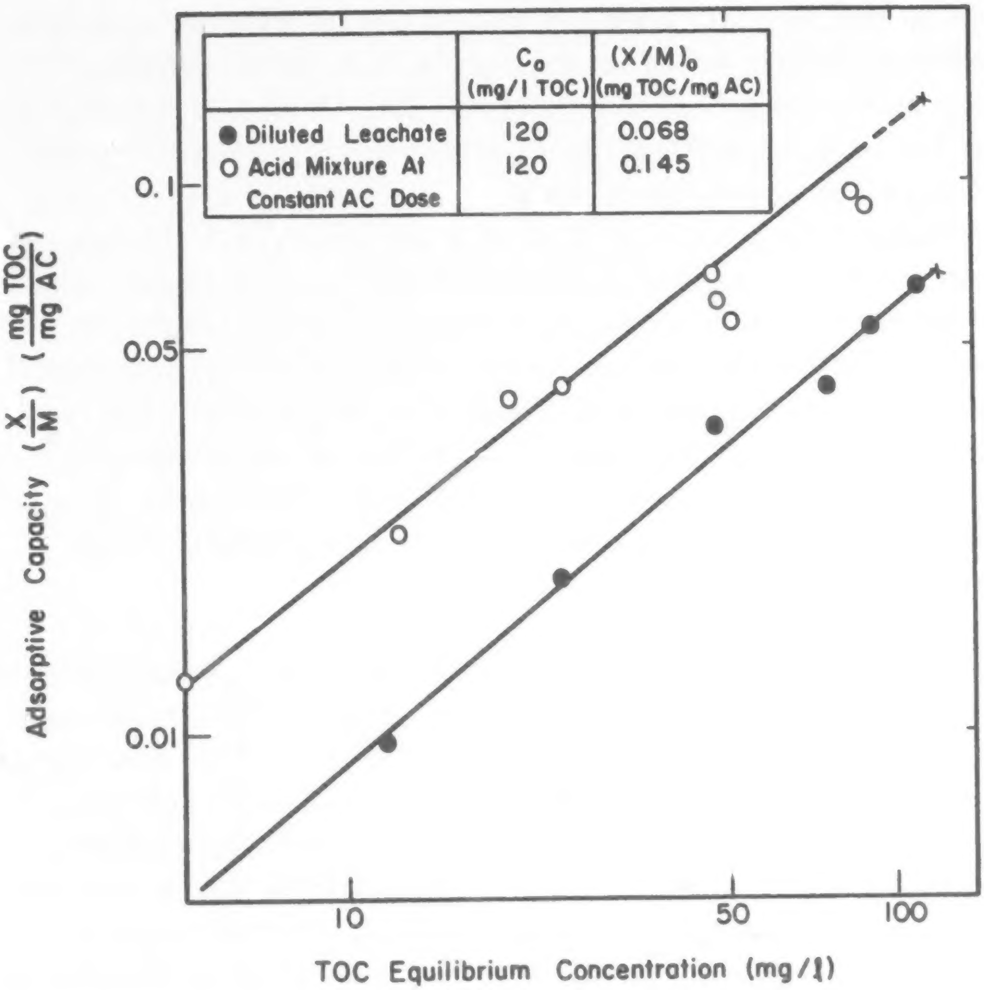


Figure 22. Activated Carbon Adsorption Isotherms with a Diluted Leachate Sample and a Fatty Acid Mixture

of the undiluted leachate, indicating that lower concentrations do correspond to higher capacities. The increase, however, is not as substantial as the increase of 6.5 times found for the biologically stabilized leachate. Since the free volatile acids comprised 52% of the organic matter in this leachate sample, an acid mixture was made having the same relative composition as the leachate sample; i.e., 20 mg/l formic, 50 mg/l acetic, 10 mg/l propionic, 50 mg/l butyric, 10 mg/l isobutyric, 10 mg/l paleric, 10 mg/l isovaleric, 70 mg/l hexanoic acid and 100 mg/l NaCl to give an initial TOC of 120 mg/l. Using this acid mixture, a maximum adsorptive capacity of 0.145 mg/l was observed 2.1 times as high as that obtained with the diluted leachate sample. This result indicates that the non-fatty-acid portion has a lower adsorption capacity than the fatty-acid fraction and that simple removal of the free volatile fatty acids, which occurs during aerobic biological stabilization, will not result in higher adsorptive capacities. Removal of the non-fatty-acid fraction and bacterial excretion or formation of refractory fulvic and humic acids may therefore be necessary before higher capacities are obtained.

Different methods of arriving at adsorption isotherms were next evaluated. While the results shown in Figure 22 for the acid mixture were obtained with a constant carbon dosage and increasing dilution of the acid mixture, the acid mixture results in Figure 23 were obtained with a constant organic matter concentration and increasing activated carbon dosages. Although the maximum adsorptive capacity in both cases was the same, the slope of the isotherm was lower using the constant carbon dosage; i.e., the value of n decreased from 1.0 to 0.79. Since the low adsorptive capacity at low equilibrium concentrations often results from the presence of a nonadsorbable fraction, dilution of the organic matter concentration and therefore reduction of the nonadsorbable fraction at a constant carbon dosage will result in a higher adsorptive capacity than will the use of an undiluted sample with increasing carbon dosages, since even very high carbon dosages will not remove this nonadsorbable fraction.

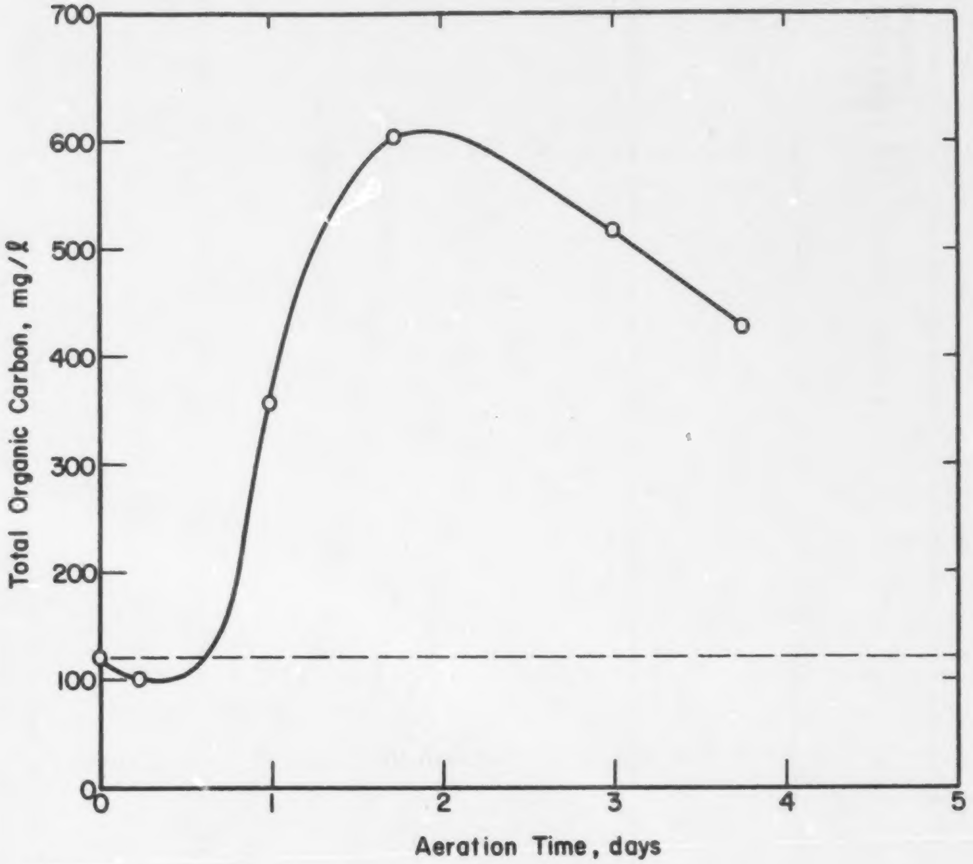


Figure 56. Results of aerobic biological polish of ozonated effluent from aerated lagoon 3 treating leachate

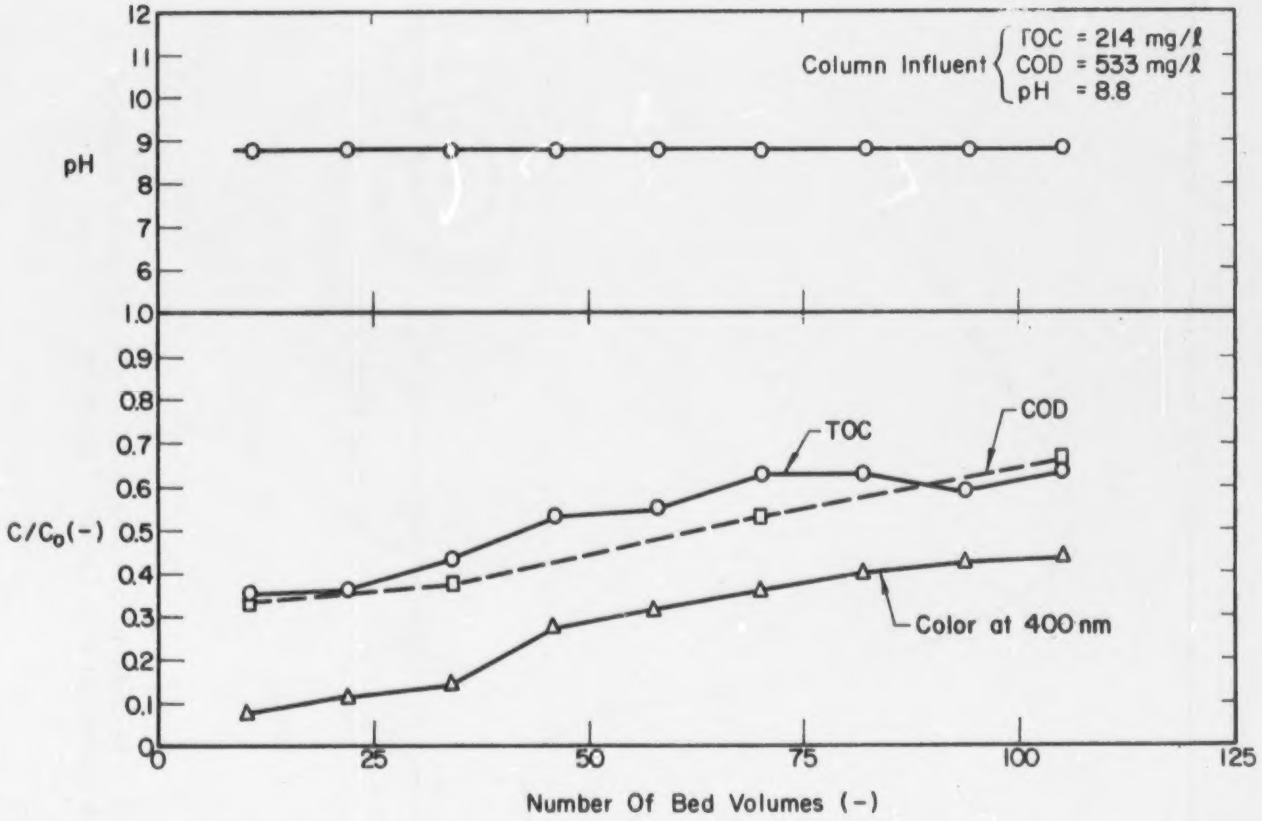


Figure 57. Activated carbon breakthrough curve for effluent from aerated lagoon unit 4 treating leachate at a flowrate of 1.76 cm/min

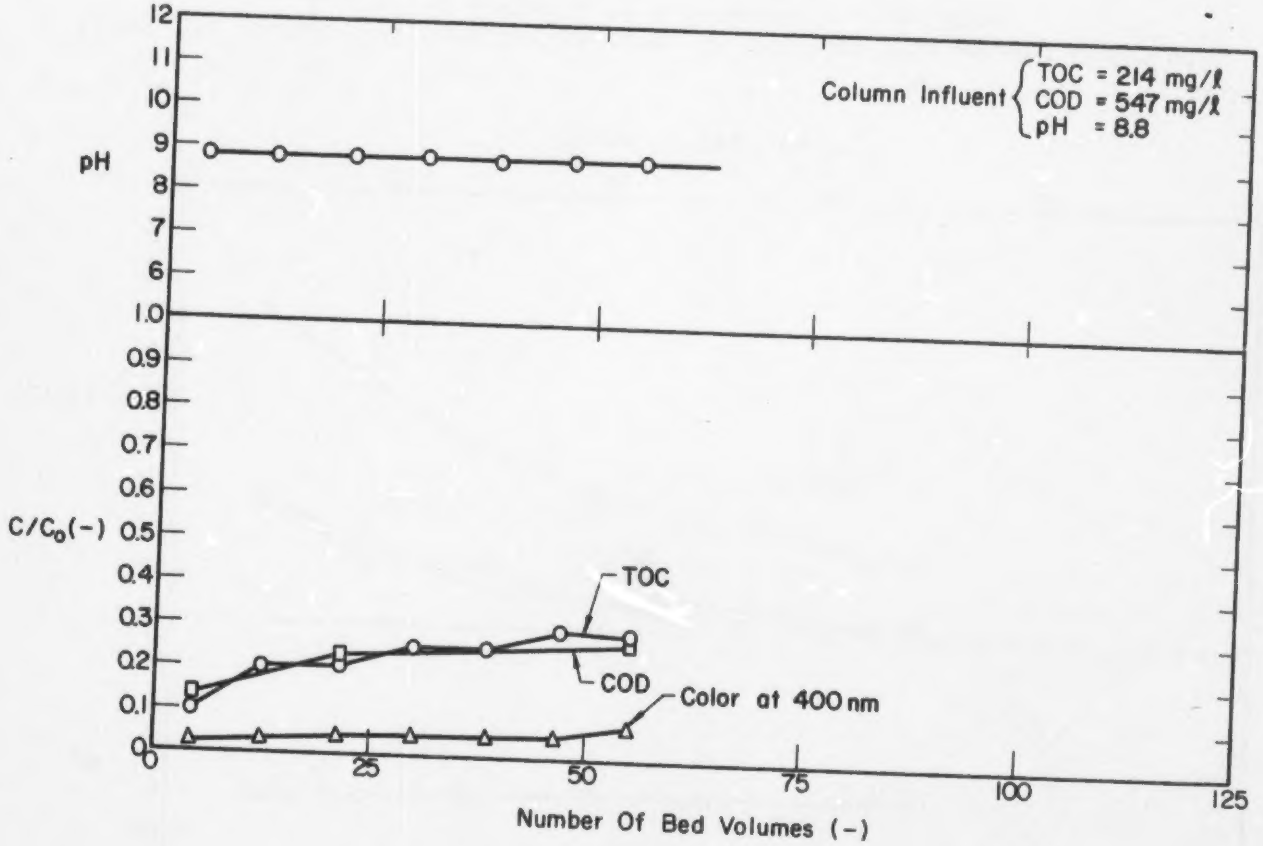


Figure 58. Activated carbon breakthrough curve for effluent from aerated lagoon unit 4 treating leachate at a flowrate of 0.35 cm/min

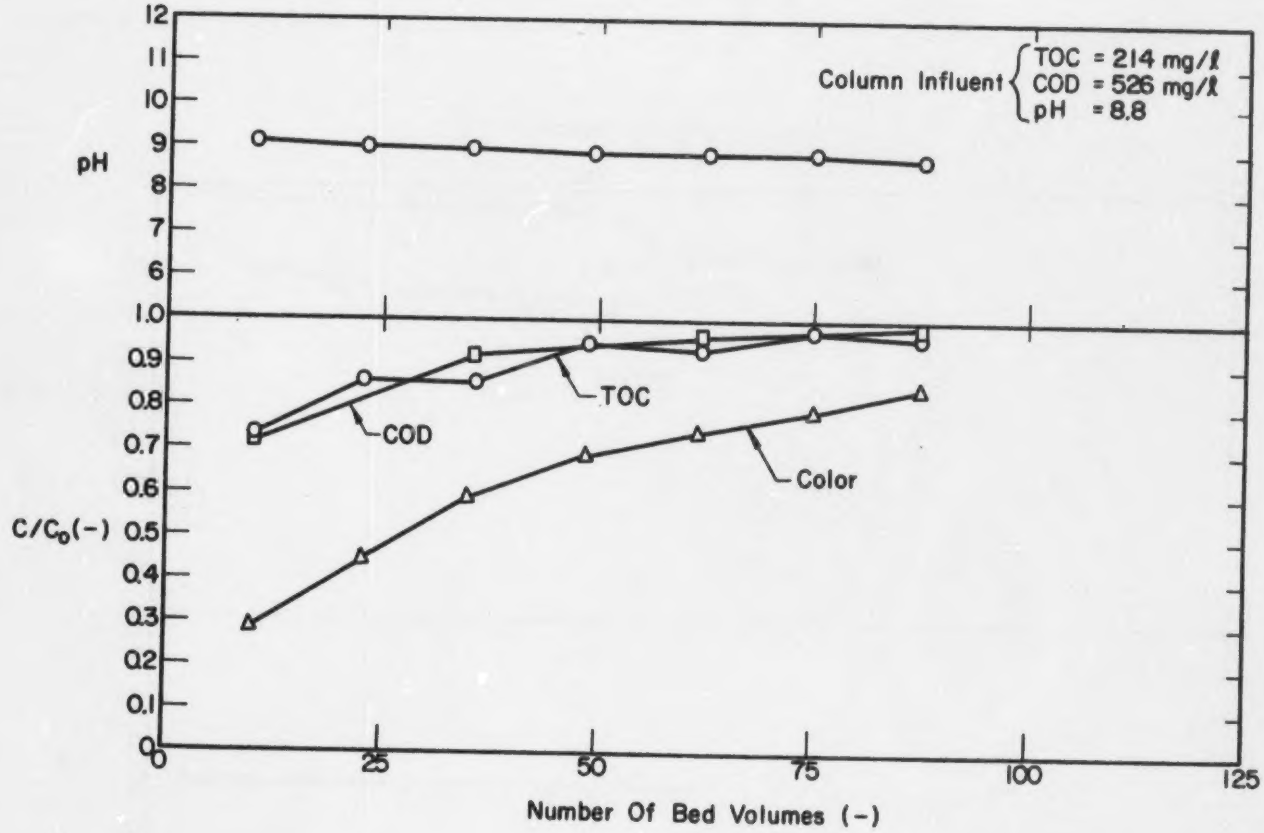


Figure 59. Duolite A-7 breakthrough curve for effluent from aerated lagoon unit 4 treating leachate, at a flowrate of 1.76 cm/min

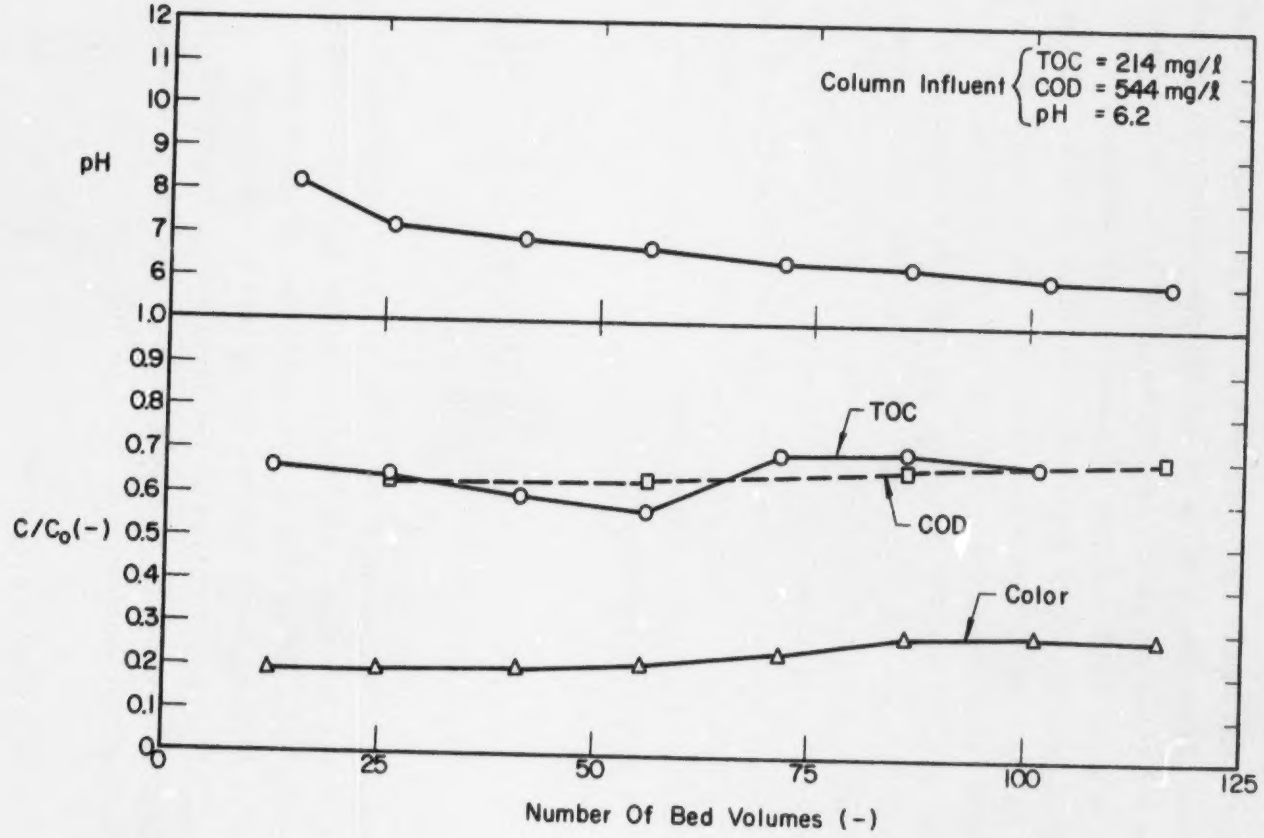
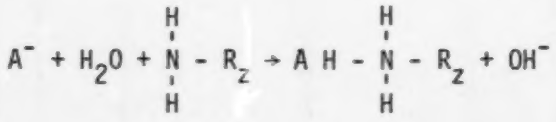


Figure 60. Duolite A-7 breakthrough curve for acidified effluent from aerated lagoon unit 4 treating leachate at a flowrate of 1.76 cm/min

respectively. When the pH was adjusted from 8.8 to 6.2, higher removals for TOC, COD, and color were observed. The initial COD removal increased from 28% to 37% as a result of the pH decrease. These removals, however, are less than the 68% removal obtained with activated carbon under similar flow conditions. Since the pK value of A-7 is approximately 6, the amine groups of the A-7 resin are mostly un-ionized at pH values much higher than 6, e.g., a pH of 9. The degree of ionization of the carboxyl groups of the organic matter in the effluent is lower at pH of 6.2 than that at a pH of 8.8. The higher removals of TOC, COD and color at pH of 6.2 may therefore result from the adsorption mechanisms of the A-7 resin in a free base form. A similar pH effect was noted by Schnack and Kaufman (1970) who used the weak base resin Duolite ES-33, with the same phenol-formaldehyde matrices as A-7 but with a pK of 4.5. Passage of the aerated lagoon effluents through the resin resulted in a pH increase from 8.8 to 9.1 and from 6.2 to 8.2. The initial increase in pH during adsorption of the organic matter onto the A-7 resin from the aerated lagoon effluent was also noted by Kim (1974). The pH increase could result from the following reaction:



$$A^- + H_2O + \overset{H}{\underset{H}{N}} - R_z \rightarrow A\ H - \overset{H}{\underset{H}{N}} - R_z + OH^- \qquad (6)$$

where A^- represents the organic anion. The last step in the preparation of the resin in the free base form involves washing with concentrated sodium hydroxide followed by rinsing with distilled deionized water which cause the protonation of the hydroxyl groups of the phenolic matrix of A-7. If the protonation of the ionized phenolic hydroxyl groups is not completed during rinsing with distilled deionized water, the following reaction would account for a pH increase:

$$R'O^- + H_2O \rightarrow R'OH + OH^- \qquad (7)$$

The pH gradually decreases to that of the influent (Figure 60) as the effluent bed volume increases, and protonation of the ionized phenolic hydroxyl groups are completed.

The breakthrough curve using the Duolite A-7 resin at the same pH of 6.2, but at a lower operating flowrate of 0.35 cm/min is shown in Figure 61. The lower flowrate resulted in an approximately 10 percent increase in color and COD removal but did not greatly enhance TOC removals indicating that less oxygenated compounds were being removed. However, the initial COD removal of 59% was still less than the 86% obtained with activated carbon under similar flow conditions. The initial pH increased more sharply at a low operating flowrate of 0.35 cm/min than at a high flowrate of 1.76 cm/min.

As strong base resins do not experience any pH effects this parameter was not investigated, and only different resin matrices were studied for this removal of organics. The main mechanisms of organic removal by strong base resins are adsorption on the resin matrix and ion exchange by the functional groups. As these mechanisms are applicable for a wide pH range, no pH adjustments are necessary. The breakthrough curves for two strong base resins with effluent from the aerated lagoon 4 are shown in Figure 62 and 63. Both of these strong base resins were operated in chloride form. Removal of TOC, COD, and color with the IRA-938 styrene-DVB matrix, was better than with the XE-279HP acrylic matrix. Since most of the organic matter in the extended aeration effluent is present as a fulvic acid-like material, containing substantial amounts of aromatic groups, a high affinity and thus stronger adsorption may be expected when the chemical configuration of the organic material and the resin matrix are similar as is the case for the aromatic styrene-DBV type resins. This affinity can be explained by the interactions of π electrons of the aromatic rings. Two clouds of electrons are formed near the aromatic ring by the π bonds between carbon atoms of the aromatic ring. The effects of π electrons affinity between aromatic compounds and the non-ionic styrene-DVB type resin obviously aids adsorption.

The salts in the effluent of these ion exchange columns did not change appreciable with either type of anion resins used. Slight increases in TDS were then experienced with the use of the strong base resins which

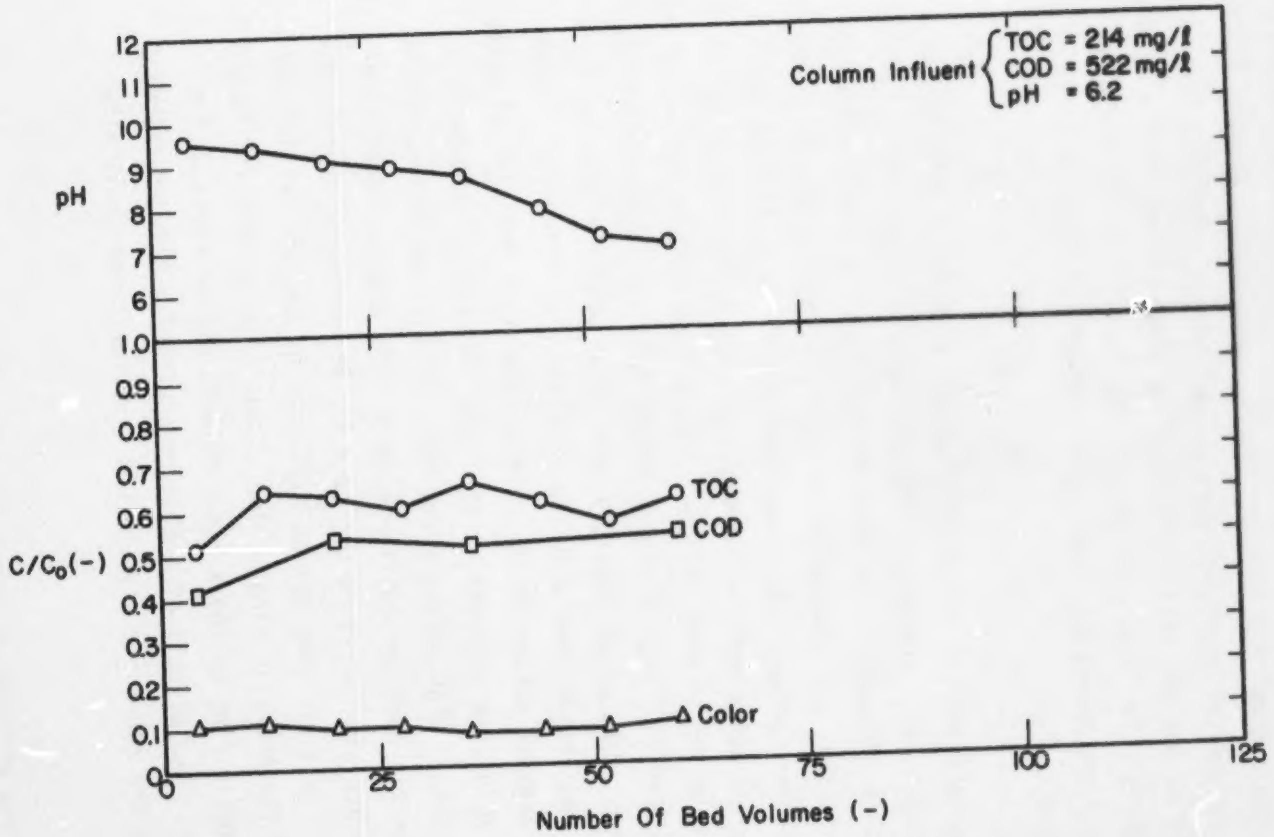


Figure 61. Duolite A-7 breakthrough curve for acidified effluent from aerated lagoon unit 4 treating leachate at a flowrate of 0.35 cm/min

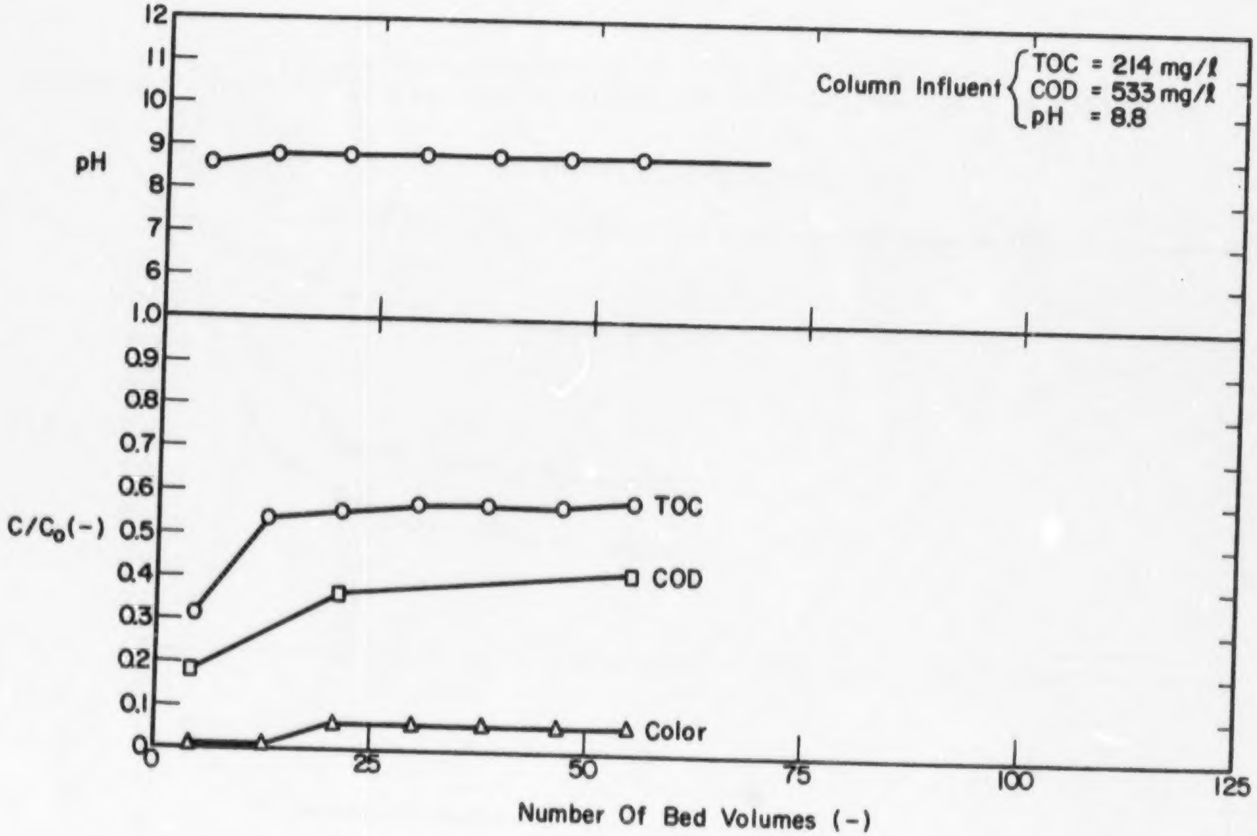


Figure 62. Amberlite IRA-938 breakthrough curve for effluent from aerated lagoon unit 4 treating leachate, at a flowrate of 0.35 cm/min

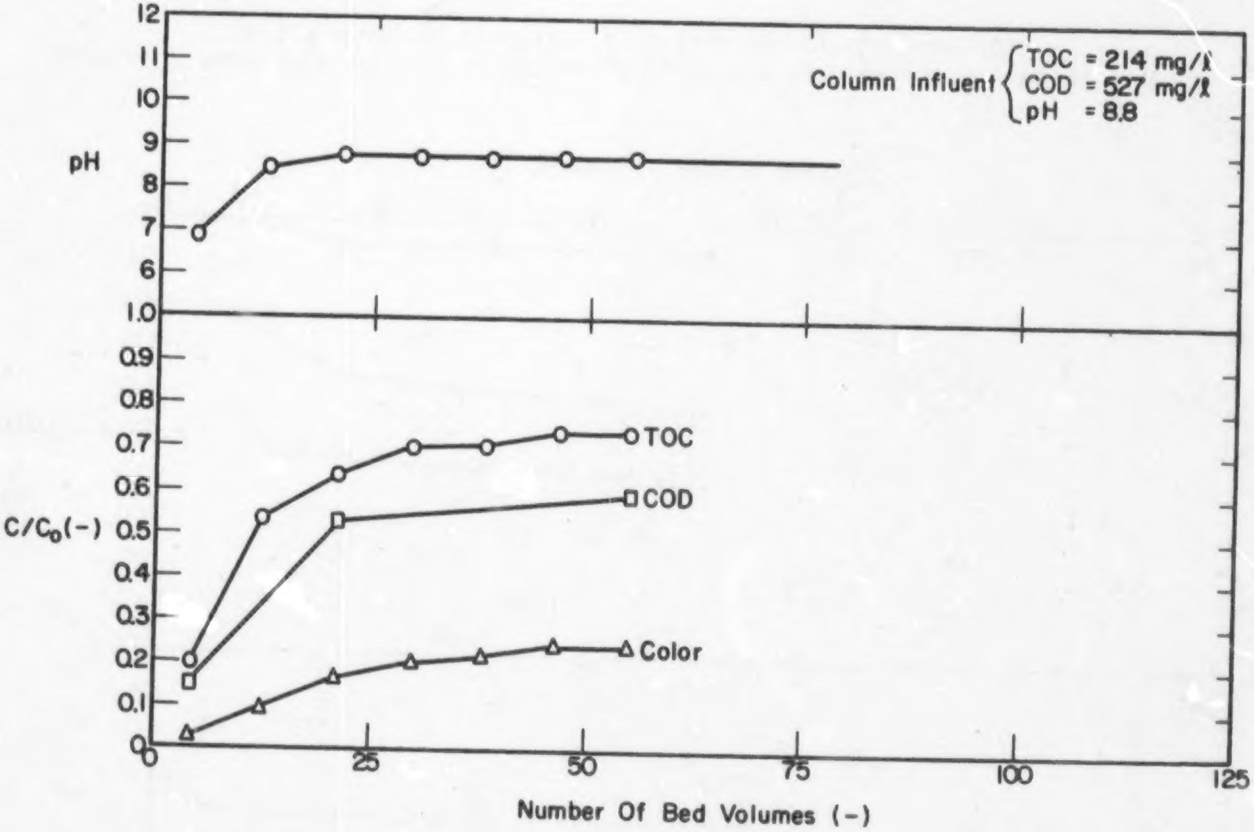


Figure 63. Amberlite XE-279HP breakthrough curve for effluent from aerated lagoon unit 4 treating leachate, at a flowrate of 0.35 cm/min

is due to the exchange of the chloride ion from the resin into the solution.

The organic removal achieved with both ion exchange and activated carbon processes are summarized in Table 14. The data collected at the same flowrate show that activated carbon gives the best removal of organic matter from aerated lagoon effluent. The next best results were obtained with the strong base resin, Amberlite IRA-938 having the styrene-DVB matrix. This resin showed a slightly greater organic removal than the weak base resin A-7, even though the effluent passed through the A-7 column was acidified.

Since relatively large and expensive thermal regeneration equipment is needed for regeneration of the spent carbon in addition to the pumping costs for transferring the carbon, synthetic resins appear to be an attractive alternative. These resins can be regenerated by inexpensive chemicals such as NaOH or NaCl.

Organic Removal in Aerated Lagoon Effluent by Reverse Osmosis

Based on the preliminary results treating raw leachate, the NS-100 reverse osmosis membranes were shown to have a better rejection of organics than cellulose acetate membranes. This is due to the distinct differences in the chemical nature of the NS-100 membrane as opposed to the somewhat more polar nature of the cellulose acetate (CA) membrane. The NS-100 membrane materials, which are less polar, have less tendency to act as proton accepters as compared with CA.

The rejection of TDS with these membranes was evaluated simultaneously with removal of organics from the aerated lagoon effluents. As shown in Table 15, both organic matter and TDS were removed effectively with the membrane process. The flux of membranes was also quite high. Membrane processes are thus an excellent method for polishing effluent from extended aeration units, activated carbon columns and ion exchange columns. Since the fouling of membranes by suspended solids is the

Table 14

Removal of Organics by Resins and Activated Carbon

Material	Flowrate	Percentage Removal After 50 Bed Volume			Influent pH	Effluent pH at 50 Bed Volume
		TOC	COD	Color		
Activated Carbon	1.76 0.35	47 71	56 74	71 94	8.8 8.8	8.8 8.8
Duolite A-7	1.76 1.76 0.35	6 42 43	6 37 48	31 80 92	8.8 6.2 6.2	8.9 6.8 7.4
Amberlite IRA-938	0.35	43	59	95	8.8	8.8
Amberlite XE-279HP	0.35	26	41	76	8.8	8.8

Table 15

Removal of Organics and Salts with the NS-100 Membrane From Effluents of the Aerated Lagoon 4, and From Effluent of the Activated Carbon- and Ion Exchange Columns

Operation Pressure = 600 psig, Temp. = 24°C

Feed Solution	TOC (mg/1)	TDS (mg/1)	% Volume Recovery	TOC in Permeate (mg/1)	% Rejection of TOC	TDS in Permeate (mg/1)	% Rejection of TDS	Flux gal/day/ft^2 (cm^3/day/cm^2)
Extended Aeration Effluent	214	6200	51.2	10.7	95	390	93.7	9.8 (4.0)
			66.2	16.6	92.2	550	91.1	9.0 (3.65)
Activated Carbon	48.2	6200	50	6.5	86.4	270	95.7	12.5 (5.1)
Ion Exchange A-7 Effluent	132.7	6200	47.6	4.7	96.5	267	95.7	12.0 (4.9)
Ion Exchange IRA-938 Effluent	118.8	6260	44.4	7.3	93.8	294	95.3	12.4 (5.0)
Ion Exchange XE-279HP Effluent	143.4	6250	48.4	8.2	94.3	310	95	11.9 (4.8)

The operating conditions for activated carbon and resins columns for treating aerated lagoon effluent were at a flow rate of 0.35 cm/min and a pH of 8.8; with the exception of the A-7 column which was run at a pH of 5.5

major limitation of this process, pretreatment of effluent from the extended aeration unit by filtration or chemical precipitation may be necessary. No significant improvement of reverse osmosis effluent quality was obtained by pretreatment of the aerated lagoon effluent by carbon and resin columns (Table 15).

Ahlgren (1971) has studied the costs of different alternatives for demineralization and concluded that cation and anion exchange methods are the only applicable for low TDS levels with concentrations less than 200 ppm. In the transition range between 200 to 2,000 ppm of TDS, electrodialysis is an attractive treatment method. Reverse osmosis is the most attractive means of demineralization. With feed water containing more than 2-00 ppm TDS. Since the TDS level in the effluent of the aerated lagoon units receiving leachate was higher than 2,000 ppm TDS, only the reverse osmosis process was considered in this study for demineralization.

The activated carbon process was further studied to treat the reverse osmosis permeate in order to obtain effluent of high quality. The influent to the activated carbon column consisting of the permeate of NS-100 membrane had an organic concentration of 16.6 mg/l TOC (33.6 mg/l COD). The results shown in Figure 64, reveal an 82% COD removal which is only slightly less than the 86% observed for the unfractionated effluent. The TOC removal, however, is considerably lower than the COD removal, indicating that highly oxidized compounds with a low COD/TOC pass through the activated carbon column.

Based on the results of the above studies, a proposed scheme for treating leachate with aerated lagoon followed by various physical-chemical methods is depicted in Figure 65. The detention time of the aerated lagoon could be varied from 10 to 30 days depending on the nature of landfill leachate being treated. The NS-100 membrane could be substituted by the duPont's B-10 Permeator (Wilmington, DE), because both of these membrane materials have comparable characteristics in terms of organic and TDS removals.

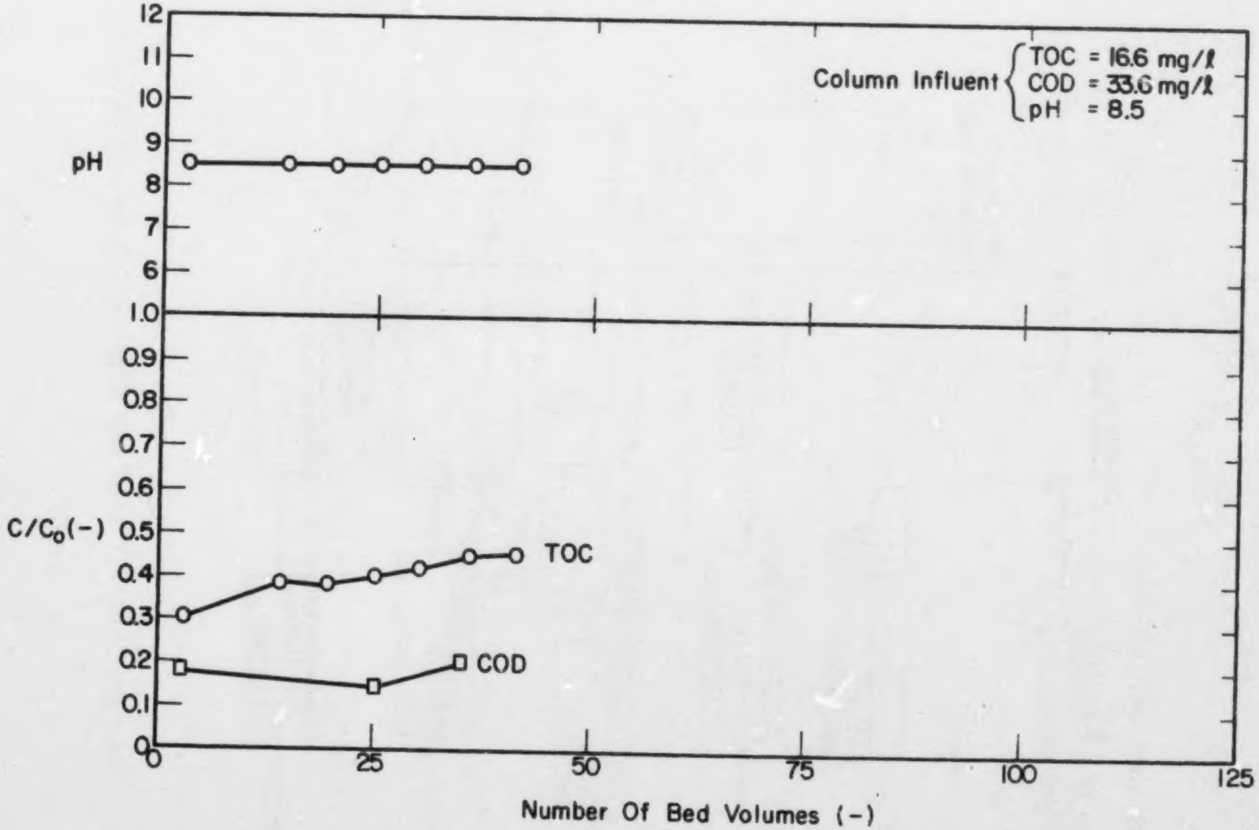


Figure 64. Activated carbon breakthrough curve for RO NS-100 membrane permeate from effluent of aerated lagoon unit 4 at a flow of 0.35 cm/min

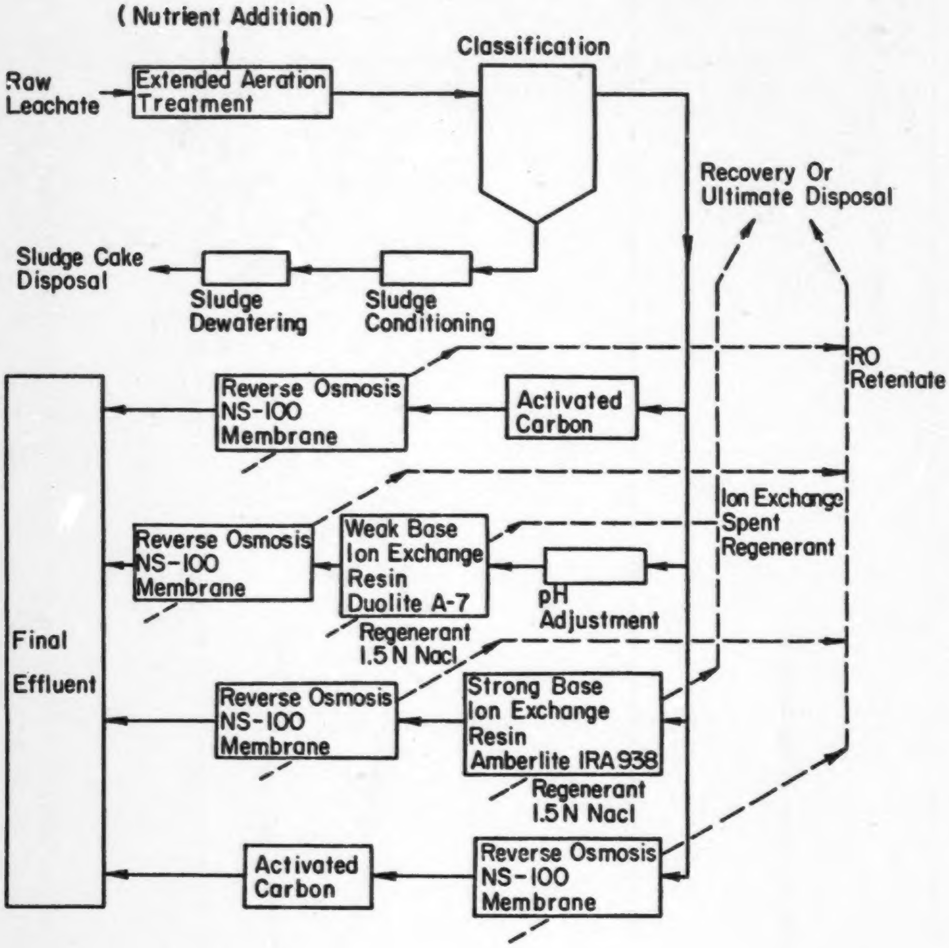

(Nutrient Addition)
Raw Leachate
Extended Aeration Treatment
Classification
Recovery Or Ultimate Disposal
Sludge Cake Disposal
Sludge Dewatering
Sludge Conditioning
RO Retentate
Reverse Osmosis NS-100 Membrane
Activated Carbon
Ion Exchange Spent Regenerant
Reverse Osmosis NS-100 Membrane
Weak Base Ion Exchange Resin Duolite A-7
pH Adjustment
Regenerant 1.5 N Nacl
Final Effluent
Reverse Osmosis NS-100 Membrane
Strong Base Ion Exchange Resin Amberlite IRA 938
Regenerant 1.5 N Nacl
Activated Carbon
Reverse Osmosis NS-100 Membrane

Figure 65. Sanitary Landfill Leachate Treatment Schematic Diagram

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V

COMBINED TREATMENT OF LEACHATE AND MUNICIPAL SEWAGE IN AN ACTIVATED SLUDGE UNIT

CONCLUSION

Laboratory study showed that a conventional plugflow activated sludge unit receiving municipal sewage could effectively treat a high strength leachate containing high concentrations of free volatile fatty acids such as acetic- and butyric acid. Directly after the leachate addition some deterioration in effluent quality of the test unit was observed; after prolonged periods, however, effluent BOD values of the test unit receiving low leachate additions were generally comparable to that of the control unit. While BOD values are not greatly affected, COD concentrations showed a gradual increase with increasing leachate addition indicating that larger quantities of refractory organics were released from the test unit. The test unit was not able to treat the high strength waste at 4% of the influent inflow rate as evidenced by high BOD effluent concentrations and deteriorating sludge characteristics. This operating failure was attributed to limiting phosphate concentrations in the influent and the relative composition of the soluble high-molecular-weight organics that tend to affect the flocculation of the sludge. A tertiary treatment unit such as activated carbon showed lower organic matter removals after addition of leachate to the municipal activated sludge unit. The decreased removal was also thought to be due to the differences in the low-molecular-weight organic matter composition. The advantage of combined treatment is that it may be the least expensive alternative as compared to treating the leachate in a separate unit at the landfill site. In addition the effluent phosphate concentration would be reduced due to the low COD:P ratio in the leachate. A disadvantage of the combined treatment is the required increase in size of the secondary clarifier while lower organic matter removals may occur in a tertiary activated carbon unit treating the effluent from the combined treatment unit.

INTRODUCTION

Solid waste landfills can have an adverse impact on the environment when leachates contaminate underlying groundwater strata or surface streams. Such impact can be controlled by reducing the quantity of leachate generated or by treating the leachate already generated. Treatment of leachate can be realized by recirculation of the leachate back into the landfill to enhance anaerobic biological removal of the pollutants, by construction of separate treatment units at the site, or by combined treatment at a municipal sewage plant. The purpose of this study was therefore to evaluate the addition of increasing quantities of leachate to a conventional plugflow activated sludge unit treating municipal sewage. Results in Chapter III indicate that high strength leachate is amenable to aerobic biological treatment. Only one earlier study evaluated the addition of leachate to a unit treating municipal sewage.

Boyle and Ham (1974) found that leachate with a COD of 10,000 mg/l could be added to domestic sewage in an extended aeration activated-sludge unit at a level of at least 5% by volume without seriously impairing the effluent quality. At greater than 5% by volume, leachate additions resulted in substantial solids production, increased oxygen uptake rates, and poorer mixed liquor separation.

ACTIVATED SLUDGE PROCESSES

The activated sludge process is a very flexible process and can be adapted to almost any type of biological waste-treatment problem. The purpose of this section is to discuss the characteristics and the applicability of both the conventional activated-sludge processes as well as some of the modifications (Metcalf and Eddy, 1972) for leachate treatment:

(a) The conventional process utilizes a plug-flow pattern with recycle of the settled sludge. The recommended operating parameters are an aeration period about 6 hours, an organic loading of about 0.2 to 0.4 mg BOD/mg MLVSS·day. The mixed liquor volatile suspended solids (MLVSS) ranges from 1,500 to 3,000 mg/l. The ratio of the volume of the recycle sludge stream to influent stream is often about 0.25 to 0.5. The sludge age is generally maintained at a value of about five to fifteen days.

(b) The complete-mix process, in which the influent waste stream is completely mixed within the total contents of the unit, has a better resistance to shock loads, and is generally applicable to biological treatment of industrial wastes (Metcalf and Eddy, 1972).

(c) The step-aeration process in which the settled sewage is introduced at several points along the aeration tank, has a lower peak oxygen demand than the conventional plugflow unit as the loading is equalized over the length of the aeration tank. Higher BOD loadings per unit aeration tank volume are therefore possible. This process is also capable of withstanding shock loads better than the conventional plugflow process.

(d) The contact-stabilization process was developed to take the advantage of the absorptive properties of activated sludge to remove colloidal, finely suspended, and dissolved organic matter in the wastes. Its value in industrial waste treatment is limited largely to wastes in which the organic matter is predominantly present as colloidal organics.

(e) The extended-aeration process, aerated lagoon and oxidation ditch processes are applicable only to small treatment plants.

(f) The Kraus process is used to treat high-carbohydrate wastes containing a low amount of N and P nutrients in combination with domestic sewage. The nutrients are added to the unit by aerating a portion of the return sludge and the digested sludge containing large amounts of N and P in a separate reaeration tank. This mixture is then combined with the remainder of the recycle sludge and returned to the aeration basin.

All of the above units can be aerated with air or with pure oxygen. The pure-oxygen process has a number of advantages, such as increased bacterial activity, decreased sludge volume, reduced aeration tank volume, and improved sludge settling (Albertson, 1970).

The present study selected the conventional plugflow activated sludge process for the combined treatment evaluation, as this process is the most commonly used at the present time to treat municipal sewage. Although the conventional plugflow activated sludge process would be subject to upsets more easily than the modifications discussed above, it is felt that if the conventional process would be able to treat the combined leachate-municipal sewage flow, the modified processes would certainly be able to treat this waste stream.

The present research simulated the conventional plugflow system by employing three completely mixed reactors in series. Theoretically, a series of an infinitive number of complete-mix reactors becomes a plug-flow reactor. However, a system with only three complete-mix reactors in series can be considered as approaching a plug-flow without much experimental error. Table 16 shows the ratio of reactor volume between the complete-mix and the plug-flow reactors by assuming first-order reaction kinetics for BOD_5 removal.

Table 16

Required Reactor Volume for a Complete-Mixed Reactor as Compared with a Plug-Flow Reactor at Various Removal Efficiencies

Number of Reactors in Series	The Ratio of Reactor Volume Vr/Vp*			
	85% Removal Efficiency	90% Removal Efficiency	95% Removal Efficiency	98% Removal Efficiency
1	2.98	3.91	6.33	12.53
2	1.67	1.88	2.32	3.10
3	1.42	1.52	1.73	1.99
4	1.30	1.32	1.49	1.70
6	1.17	1.25	1.30	1.41
8	1.14	1.15	1.20	1.29
10	1.10	1.13	1.17	1.23
	1.0	1.0	1.0	1.0

*Vr = Volume of a series of complete-mix reactors
Vp = Volume of the plug-flow reactor

COMBINED TREATMENT OF HIGH STRENGTH WASTE AND MUNICIPAL SEWAGE

Several studies have pointed out advantages of combined treatment of an industrial waste and municipal sewage as compared to separate treatment of the two waste streams. The significant savings in capital and operating costs is often mentioned as its largest advantage (City of Dallas, 1971). Longdon (1969) further pointed out that combined treatment reduced the foaming and bulking of a municipal activated sludge plant receiving yeast wastes. In fact many industrial wastes such as those from meat packing plants, cotton mills, metal industries (El-Gohary, 1971) pharmaceutical industries (Andersen *et al.*, 1971), citrus processing plants (Eidsness *et al.*, 1971), drying industry (Hashimoto *et al.*, 1972) and papermills (Clingenpeel and Jones, 1974) are amenable to combined treatment.

In several instances, however, it was necessary to either modify existing treatment plants or to adapt the treatment plant operation to the specific waste. Poon (1970), for example, showed that combined treatment was successful when not more than one part of a high strength nylon waste was added to seven parts of municipal sewage. Brosig *et al.* (1971) indicated that 90% BOD removal was only realized at hydraulic retention times as high as 9 hours. Often treatment plants have to be converted to accept the industrial waste. A conventional municipal activated sludge plant was converted to a contact stabilization plant in order to treat a nitrogen deficient corn products waste (Niles and Etzel, 1971). Pilot plant investigations of the conventional, Kraus and contact stabilization process resulted in the selection of the latter process for combined treatment of municipal wastewater and weak effluents of four paper mills (Vockel *et al.*, 1974). It was further noted that nutrient addition and chlorination of the return sludge were requred.

Previous studies at the University of Illinois showed that a plugflow activated sludge unit treating municipal sewage could effectively degrade a pretreated industrial wastewater from a chemical industry at a waste to sewage ratio of as high as 2.5 to 1. Although the effluent COD values showed a substantial increase as compared to the control unit, neither the effluent BOD nor the settleability of the sludge showed any change when the F/M ratio of the unit remained constant. The COD removal in activated carbon columns treating the effluent of the combined activated sludge unit was also not affected by the waste additions (Chian et al., 1976). The present study used the same activated sludge units but evaluated a landfill leachate waste stream of a substantially higher strength and of a less biodegradable nature than the industrial wastes. Using a similar solid waste leachate stream with a COD of 10,820 mg/l, Boyle and Hqm (1974) added increasing volume percentages of leachate to a batch operated extended aeration unit with a 24 hour detention time treating municipal sewage resulting in an increased organic loading of the units from 0.04 to 0.5 kg BOD/kg MLSS day. They concluded that the units were not significantly affected below a 5% addition of leachate, corresponding to an organic loading of 0.15 kg BOD/kg MLSS day. As they varied two factors at the same time, i.e., organic loading and percentage of leachate addition, it is difficult to conclude the impact of each factor. The present study therefore used a different experimental design in which the loading to unit was kept constant while the percentage of leachate addition was gradually increased. The effluent of both the test and the control unit had to meet Illinois effluent standards of a BOD not to exceed 10 mg/l and a suspended solids concentration not to exceed 12 mg/l. Cities with more than 500,000 inhabitants or cities that discharge into lake Michigan should not exceed 4 mg/l BOD or 5 mg/l suspended solids. Furthermore the effluent ammonia-N concentration should not exceed 2.5 mg/l in the summer, and 4 mg/l the remainder of the year, while phosphorous should not exceed 1 mg/l and TDS should not exceed 750 mg/l.

As the combined treatment requires an adequate nutrient balance for the activated sludge, determination of the N and P content of different leachates was made. The compositions of leachate samples from different sanitary landfills reveal a large variation in concentration of different constituents (Table 17). The characteristics of the leachate produced from a given landfill depend upon such variables as composition of the landfill material, environmental conditions, and age of the landfill. Morgan et al. (1973) recommended that the optimum nutrient ratio for the conventional activated-sludge process should be BOD_5:N:P = 100:5:1. These ratios are not fixed but depend upon both the sludge age, and the operating conditions of the activated sludge system. The average concentration of nutrients in leachate are 10,244 mg/l of BOD_5, 215 mg/l of N and 24.61 mg/l of P which would result in average ratio for BOD_5:N:P of 100:2.09:0.24. This indicates that the leachate is deficient in both nitrogen and phosphorus. The municipal sewage on the other hand contains too much nitrogen and phosphorus relative to BOD_5 materials, thus sewage treatment plants have experienced difficulty in removing these nutrients. Furthermore high nitrate concentrations often cause operating problems in the secondary clarifier as denitrificstion and formation of nitrogen gas bubbles may prevent adequate sludge settling. The combined treatment of leachate with sewage would provide, at least a partial solution to both of these problems. Since the excess nitrogen and phosphorus present in the sewage can compensate for the deficiency in nutrients in the leachate, the potential financial savings resulting from the elimination of requirements for nitrogen and phosphorus removal processes may offset some of the additional costs required for expanding the system to treat leachate.

The analysis of leachate samples from sanitary landfills showed very high concentrations of metals and total dissolved inorganic solids (TDS) (Table 17). Many of the metals are expected to precipitate in the aeration tank as metal hydroxide or calcium carbonate under aerobic and alkaline conditions. The TDS is not expected to present problems in the operation of the treatment plant when a high dilution ratio with the sewage is selected.

The anaerobic-sludge digestion is the most common means of treating the waste-activated sludge. Metals that are concentrated by the biological sludge in the aeration tank are often released during anaerobic digestion.

Table 17

Composition of Leachate Samples Collected from Eleven Different Sources (Chian and DeWalle, 1976)

Source Parameter (mg/l)	UI Lysimeter	Range	Average
COD	49,300	81.10-71,680	15,670
TOC	17,060	70.00-27,700	5,567
BOD_5	24,700	3.90-57,000	10,244
Biocarbonate Alkalinity (CaCO)	668	142.00- 3,520	914
pH	5.13	5.09- 7.25	6.13
Conductivity (μmho/cm)	13,700	978.00-16,800	6,234
ORP (mV)	-60	(-220)-(+163)	-11.36
Turbidity (JTU)	75	23.00- 270	91.31
SS	139	8.90- 923	264
FSS	92.5	7.50- 901	193
TS	33,989	911.00-55,348	12,559
FS	15,586	812.00-22,895	5,704
Org-N	544.7	3.20- 945	135
NH_4-N	392.6	1.40- 1,028	211
NO_3-N	0.5	0.40- 10.25	3.93
NO_2-N	Trace	Trace - 0.19	0.03
Total-P	21.5	0.50- 98	24.61
Ortho-P	6.5	0.25- 85	16.05
SO	1,110	7.40- 1,558	284
Cl	1,480	60.20- 2,467	720
Ca	3,750	76.00- 3,900	961
Mg	650	35.00- 1,140	334
Fe	2,200	0.50- 1,046	402
Na	1,360	37.50- 1,580	391
K	1,140	35.00- 2,300	527

The ferric ion is reduced to ferrous ion, and precipitated with sulfide, phosphate, or carbonate. Malhotra, et al. (1971), for example, found that the pH, alkalinity, volatile acids, and the percentage of reduction of volatile solids in test digesters used for digesting sludges containing iron phosphates were not different from those in control digesters. The addition of ferrous-iron in the feed sludge up to a maximum level of 5.5% on a dry solids basis did not upset the digestion process. However, the thickened waste-activated sludge containing the precipitated iron phosphates resulted in significant releases of phosphate during digestion. Singer (1972) indicated that the release of phosphate from anaerobic digesters is limited by the concentration of ferrous iron, which forms solid ferrous phosphate or vivianite, while retention as solid calcium phosphate [$Ca_3(PO_4)_2$] or hydroxyapatite [$Ca_5(PO_4)_3OH$] was not thought to be the major mechanism. Thomas (1972) reported that the results obtained from eight wastewater treatment plants showed that the phosphate precipitated with ferric chloride did not appear in the supernatant during the digestion of activated sludge containing iron phosphate. The above results, therefore indicate that although addition of iron will not upset the anaerobic digestors, it may cause significant release of phosphates during the digestion process.

Based on the above considerations, an evaluation was made of a conventional plugflow activated sludge unit maintained at a constant loading but receiving increasing volumetric amounts of leachate. The unit was also tested with a constant volume addition of leachate but at increasing loadings. During leachate additions the effluent quality was monitored for nutrients to ensure adequate growth. The sludge was evaluated for its settling properties to determine any impairment that might be introduced as a result of leachate addition. The anaerobic digester receiving waste sludge from the combined biological unit was evaluated for potential phosphate recycle.

MATERIALS AND METHODS

The continuous flow units employed in the present study consisted of a primary clarifier, activated sludge units and secondary clarifiers (Figure 66). A 190 liter (50 gallon) capacity primary clarifier was operated on a batch basis in which a Moyno pump (Robbin and Meyer, Arlington Heights, IL) was turned on fifteen minutes every hour to replace the volume in the clarifier with sewage pumped from the municipal sewer. The sewage was introduced into the primary sedimentation tank from the bottom, and the suspended solids that settled in the tank were flushed out every hour for fifteen minutes through the overflow. The sand particles that settled on the bottom of the tank were removed manually every few months. The clarified sewage was drawn from the middle of the tank and delivered to the aeration tank by the Moyno feed pumps. A lever switch was installed on the primary clarifier as a safety device. When the level of sewage in the tank dropped to a point somewhat above the outlet to the Moyno feed pumps, the feed pumps were shut off automatically to prevent wearing by running dry.

The aeration basins with a total effective volume of 60 liters consisted of three completely mixed compartments in sequence. A weir was provided on each of the partitions to allow overflow to the succeeding compartment. The design of the air supply system is shown in Figure 67. An air filter was installed upstream of the air regulator for removing particulate matter from the air line (the particulates might otherwise clog the air supplying system). The air line pressure was controlled by a regulator, and the distribution of air to the diffusers was controlled by six airflow meters. The diffusers were made of perforated polyethylene instead of the more conventional porous stone. Plugging of the stone air diffusers through biological growths had been experienced in early runs.

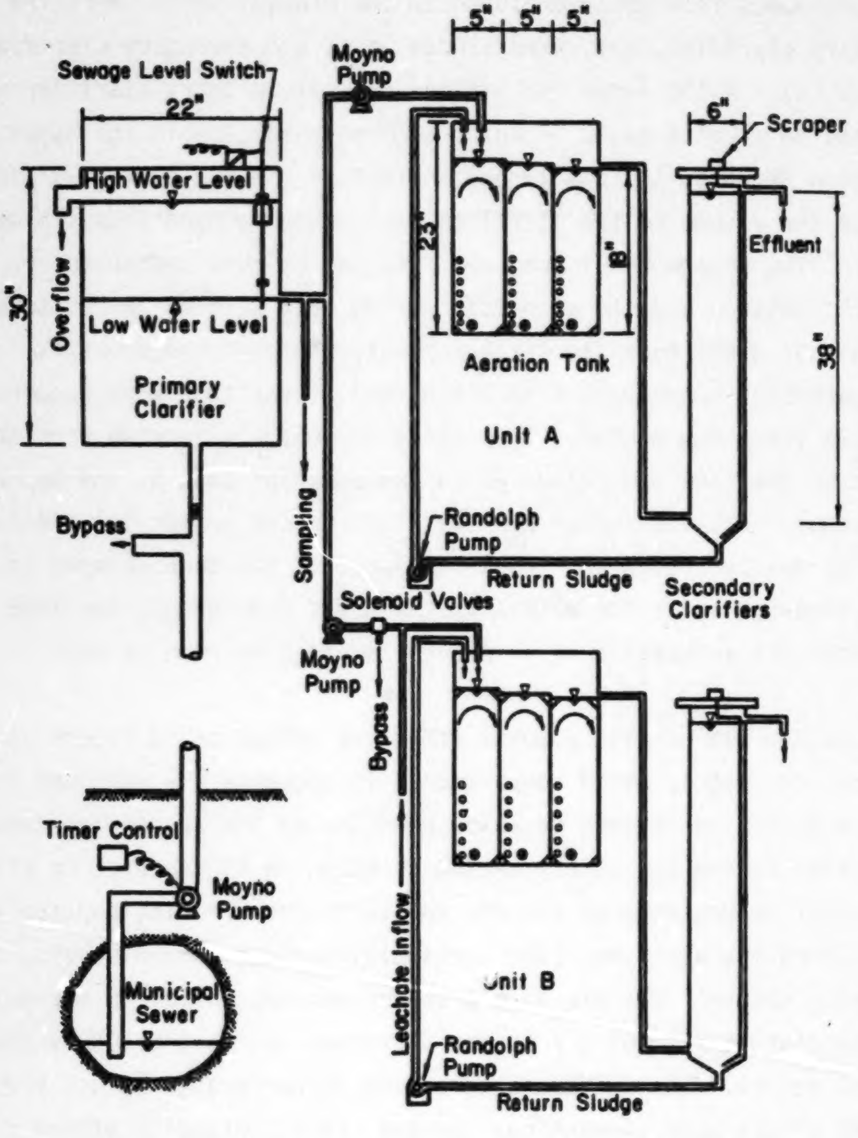
5"
5"
5"
Moyno Pump
Sewage Level Switch
22"
6"
Scraper
High Water Level
30"
Overflow
23"
18"
Effluent
Low Water Level
Aeration Tank
38"
Primary Clarifier
Unit A
Sampling
Bypass
Randolph Pump
Return Sludge
Secondary Clarifiers
Solenoid Valves
Moyno Pump
Bypass
Timer Control
Moyno Pump
Leachate Inflow
Municipal Sewer
Unit B
Randolph Pump
Return Sludge

Figure 66. The Hydraulic Flow System of the Plugflow Activated Sludge Pilot Plant

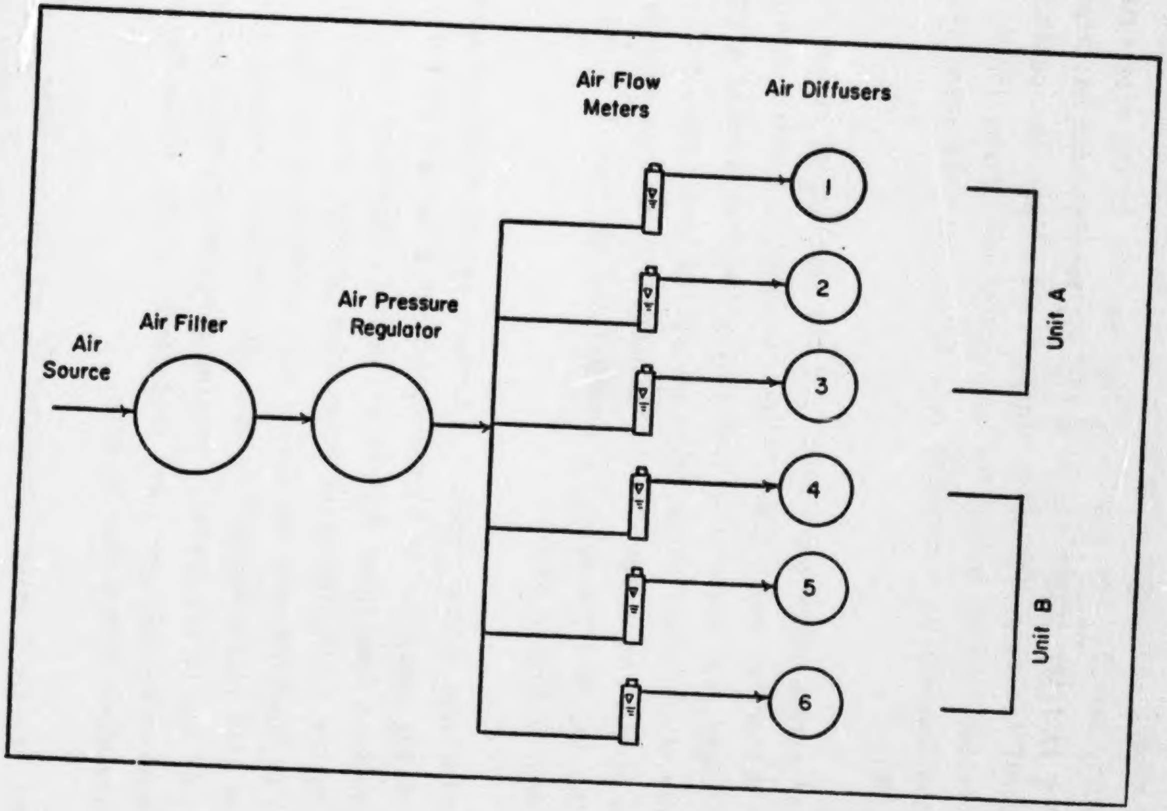
Air Source
Air Filter
Air Pressure Regulator
Air Flow Meters
Air Diffusers
1
2
3
4
5
6
Unit A
Unit B

Figure 67. Airflow System for the Activated-Sludge Pilot Plant

The secondary clarifiers with a volume of 17.5 liters were designed for a detention time of 70 minutes at a flowrate of 250 ml/min and a surface over flow rate of 2.28 liter/cm^2·sec (285 gpd/ft^2). A rotating scraper was installed to minimize any wall effect from the sedimentation units. The thickened sludge was pumped with peristaltic Randolph pumps (Randolph Company, Houston, Texas). The leachate, that was fed to the test unit, was stored in a 19 liter (5 gallon) polyethylene bottle which was kept at 5°C. An electrolytic pump, producing hydrogen and oxygen, was connected to a rubber bladder located in the leachate container. Expansion of the bladder fed the leachate at a constant rate to the test activated sludge unit (Figure 68).

The wasting of excess activated sludge, and the sampling of sewage were performed by Masterflex pumps (Cole Palmer, Chicago, IL) which were controlled by a timer, and operated automatically for five minutes every hour. A three-way solenoid valve, also controlled by a timer, was installed to bypass the sewage flow to the test unit for the purpose of controlling the feedflow rate. A schematic of the overall electrical system is shown in Figure 69.

The activated-sludge system requires a certain amount of maintenance. The tubing of the pumps had to be replaced after a certain period of operation, varying from three days to six months, depending upon the flow rate. The rubber tubing (Matheson Scientific Company, Elkfron Village, IL) used in be Randolph pump had a life span of three to six days. The Tygon tubing used in the Masterflex pump (Cole Palmer, Chicago, IL) had a life span of one to six months. Packing rings on the Moyno Pumps had to be replaced every half year, and replacement of the Stator Assembly was necessary about once a year or more.

The anaerobic sludge digesters consisted of two reactors made of Plexiglas 26.6 cm diameter and 45.8 cm in height having a volume of approximately 24 liters (Figure 70). Each reactor was fitted with a stainless steel helical worm stirrer, equipped at the bottom with a scraper extending

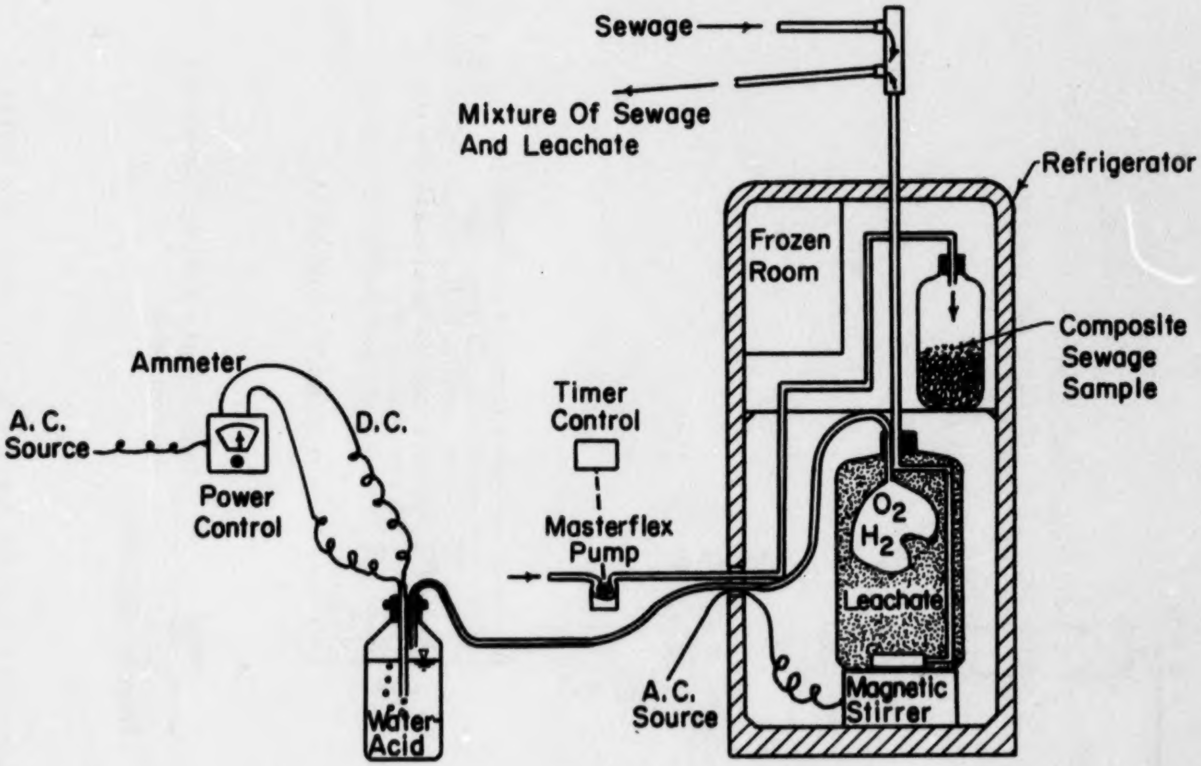
Sewage
Mixture Of Sewage And Leachate
Refrigerator
Frozen Room
Composite Sewage Sample
Ammeter
A. C. Source
D.C.
Power Control
Timer Control
Masterflex Pump
O_2
H_2
Leachate
A. C. Source
Magnetic Stirrer
Water
Acid

Figure 68. Leachate Feeding and Automatic Sampling Systems

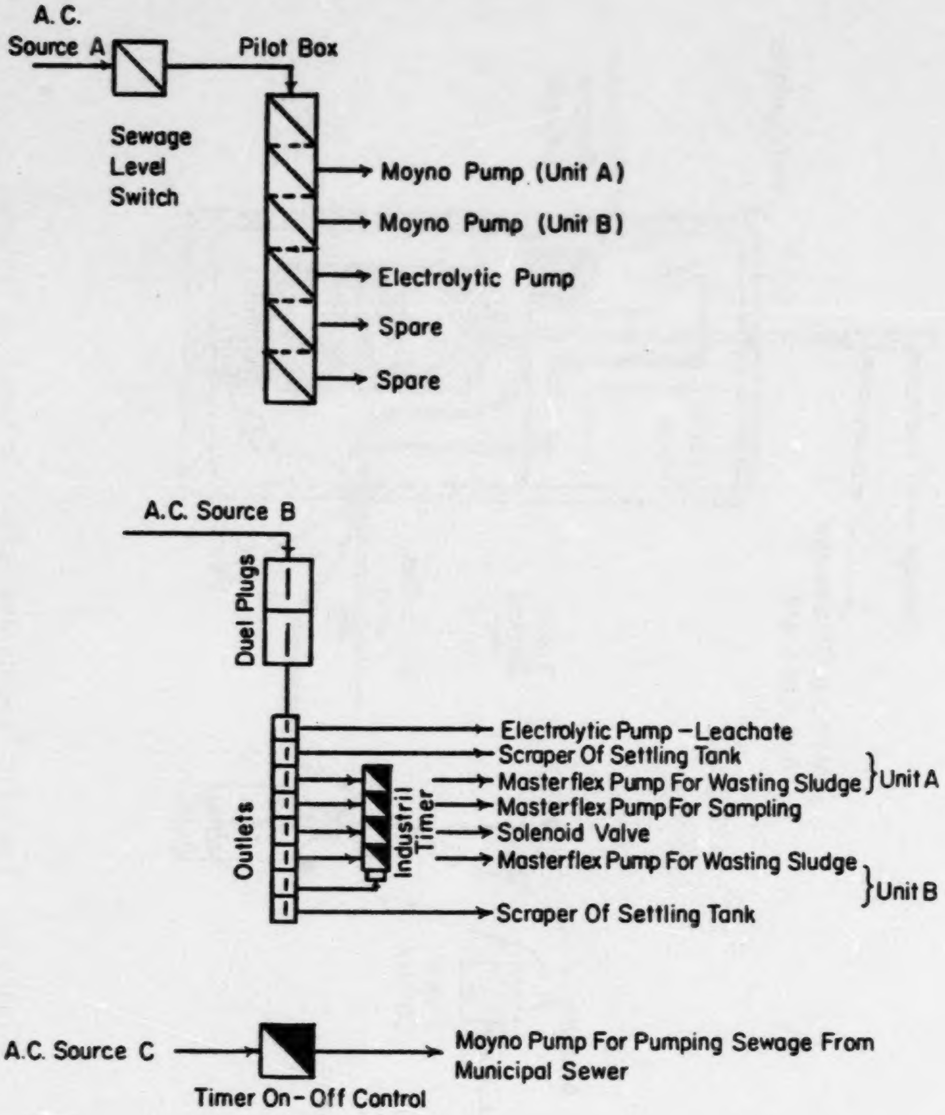
A. C.
Source A
Pilot Box
Sewage
Level
Switch
Moyno Pump (Unit A)
Moyno Pump (Unit B)
Electrolytic Pump
Spare
Spare
A.C. Source B
Duel Plugs
Outlets
Industril Timer
Electrolytic Pump – Leachate
Scraper Of Settling Tank
Masterflex Pump For Wasting Sludge
Unit A
Masterflex Pump For Sampling
Solenoid Valve
Masterflex Pump For Wasting Sludge
Unit B
Scraper Of Settling Tank
A.C. Source C
Timer On-Off Control
Moyno Pump For Pumping Sewage From
Municipal Sewer

Figure 69. Electrical Systems for the Activated-Sludge Units

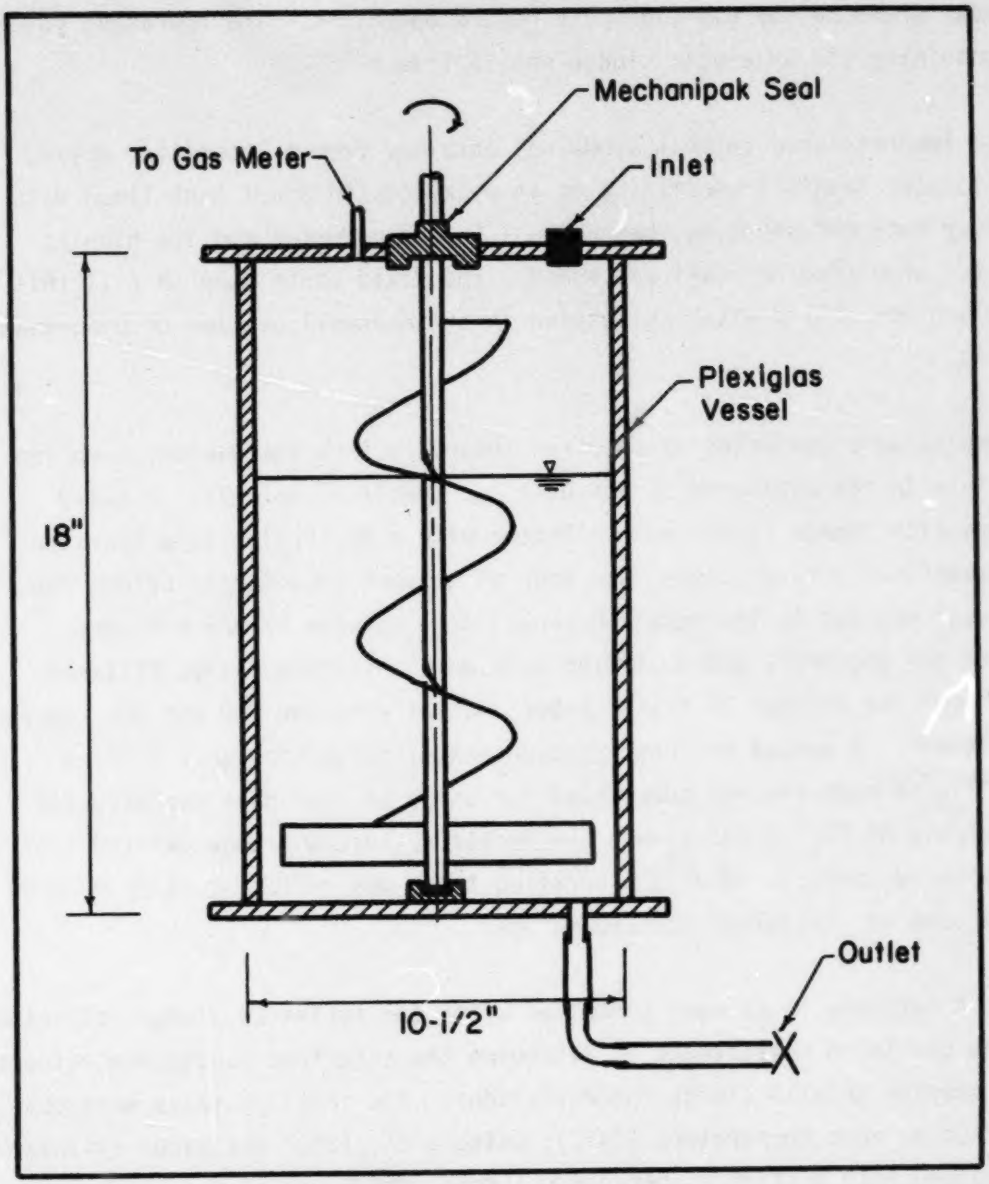
Mechanipak Seal
To Gas Meter
Inlet
Plexiglas Vessel
18"
10-1/2"
Outlet

Figure 70. Schematic of the Anaerobic Digesters

almost the whole diameter of the reactor. The stirrer was operated continuously at 60 revolutions per minute. All reactors were tested under pressure for gas tightness before operation. The operating volume containing the anaerobic sludge was 15 liters.

The leachate used in this study was obtained from a laboratory scale, simulated landfill consisting of an epoxy-coated steel tank lined with heavy duty PVC sheeting, measuring 1.5 m in diameter and 3 m high to which simulated rainfall was added. The solid waste used to fill this column was milled after collection in the Hartwell section of Cincinnati, Ohio.

Samples were collected at specific intervals from the various sampling points in the activated sludge unit for specific analysis. A daily composite sewage sample was collected with a Masterflex pump operated automatically five minutes per hour at a point immediately before the sewage was fed to the aeration tank. Grab samples of the effluent from the secondary sedimentation tank were collected daily, filtered through the Whatman #4 filter paper and analyzed for COD and BOD_5 concentrations. A second effluent portion was filtered through a 0.45 μm Millipore membrane and composited for three or four days and used for analysis of PO_4^{-3}-P and k_j-N. The excess activated sludge, wasted from the third compartment of the aeration tank, was collected daily weighed and used to calculate the sludge age.

Batch settling tests were conducted using the activated sludge collected from the third compartment to determine the interface subsidence velocities at varying initial sludge concentrations. The settling tests were conducted at room temperature (24°C), using a one-liter graduated cylinder equipped with a stirrer operated at 1 rpm. The slope of the linear portion of the settling curve was used as the interface subsiding velocity, at a given initial sludge concentration

Both the test and control activated sludge unit were initially operated at a food-to-micro organism (F/M) ratio of 0.3 kg BOD_5 removed/kg MLVSS·day, while the volume of leachate added was gradually increased from 0.5% to 1%, 2%, 3% and 4%. In order to maintain both a constant F/M ratio and a constant MLVSS concentration, the hydraulic detention time of the test unit was gradually increased. In the second phase of the study the volume percentage of added leachate was kept constant at 2% while the F/M ratio was increased from 0.3 to 0.6 and 1.0, respectively. The anaerobic digestors were operated in a semicontinuous process with a theoretical detention time of fifteen days which was maintained by withdrawal of 1 liter of digester content and addition of one liter of fresh sludge the solids of which consisted of approximately 50% primary sludge and 50% activated sludge from the 0.3 F/M leachate unit. The primary sludge was collected from the Sanitary District of Urbana.

RESULTS AND DISCUSSION

Sewage Analysis

During the year-long study which started on September 1973, a total of 74 composite sewage samples were analyzed for their BOD_5, COD, P and N concentrations. The distribution of the analytical results for the BOD_5 is shown in Figure 71 which indicates that the highest frequency was observed in the range of 80 to 100 mg/l; the maximum was 464 mg/l, the minimum 40 mg/l and the average 214 mg/l. As sewage strength showed day to day variation, while the activated sludge concentration and waste was maintained constant, the loading of the unit also experienced some daily variation. However, when averaged over a longer period of time the average F/M ratio was indeed 0.3 mg BOD_5/mg MLVSS·day.

Hydraulic Flow Regimen of the Aeration Unit

Tracer studies using methylene blue were performed to characterize the actual flow pattern in the aeration tank while aeration was supplied for mixing. Figure 72 shows the normalized concentration of tracer versus time in each of the three completely-mixed compartments connected in series through the weirs. Results of experimentally-determined concentration versus time were compared wiht the theoretical values, as shown by the dotted lines in Figure 72. The theoretical values were calculated based on the equation given below:

$$\frac{C_n}{C_o} = \left(\frac{Q}{V}\right)^{n-1} \left(e - \frac{Q_t}{V}\right) \frac{1}{(n-1)!}$$

C_n = Concentration of tracer in chamber n at time t (mg/l)

C_o = Initial concentration of tracer at time zero in chamber 1 (mg/l)

Q = Flow rate through the system (ml/min)

V = Volume of the tank (ml)

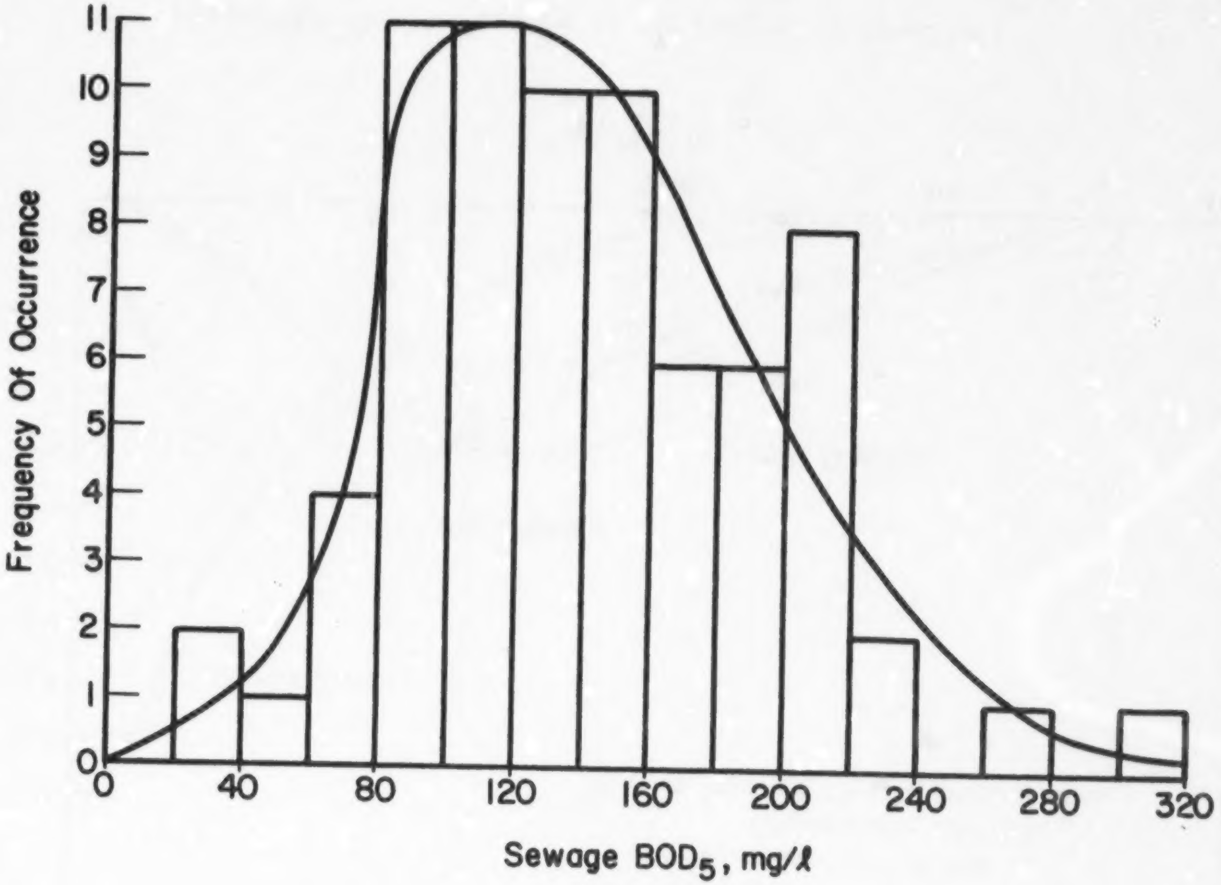

Figure 71. The distribution of BOD$_5$ concentration in the daily composite sewage samples

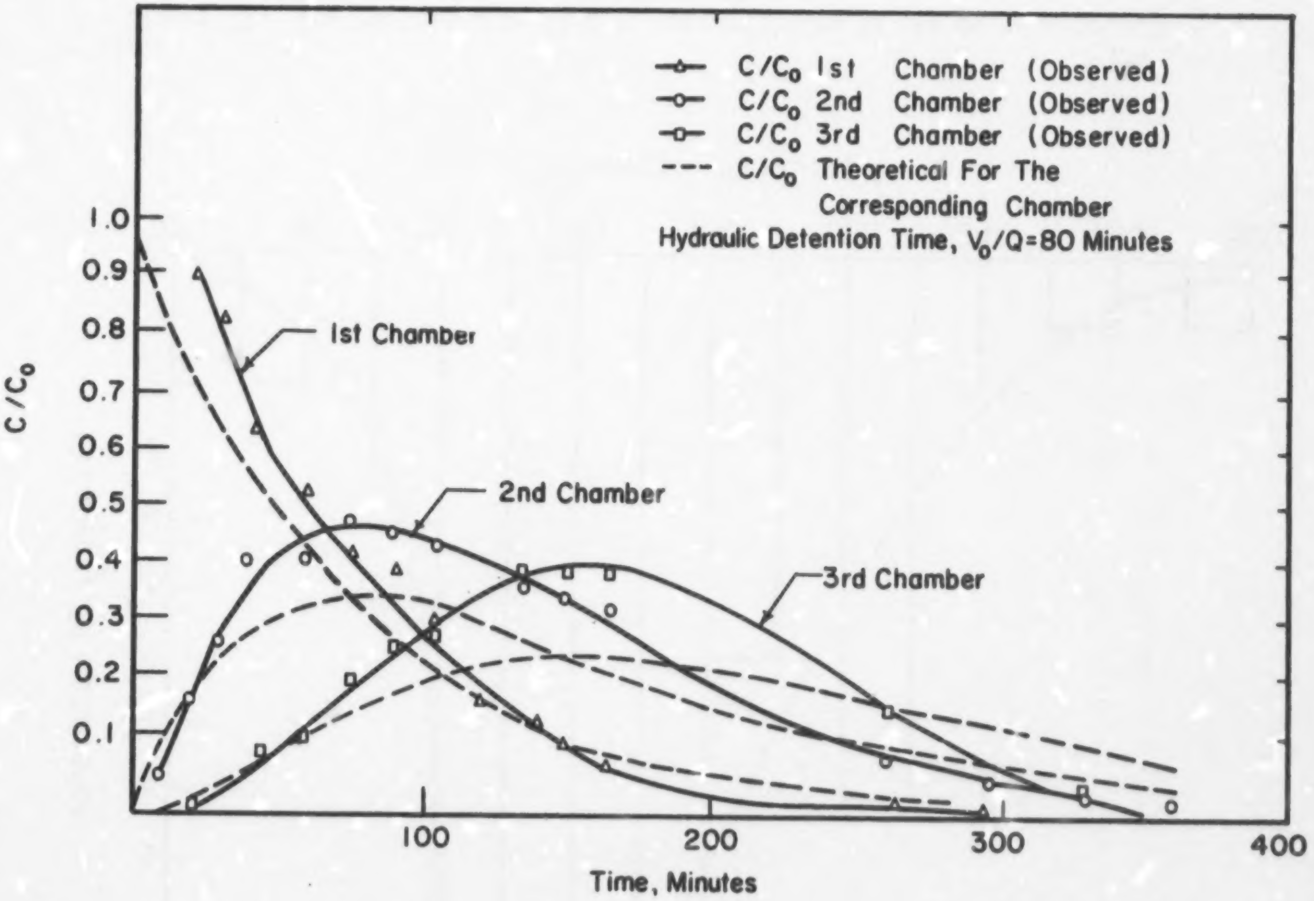

Figure 72. The flow pattern of the designed aeration tank

The results indicate that the initial wash-out of the first compartment is less rapid than theoretically predicted, indicating some incompletely mixed corners in the unit. The maximum concentration in the second compartment was about 30% higher while that in the third compartment was 55% higher than predicted from theoretical considerations, indicating partial plug-flow conditions. However the time preiod that the maxima in each of the C/C_0 curves occurred agreed with that predicted from theoretical considerations. The hydraulic flow regime is greatly affected by the degree of mixing of theunit, which in turn depends on the amount of aeration applied to each of the aeration chambers.

During the operation of the activated sludge unit an airflow rate of 0.5 liter of air per liter of aeration tank volume per minute was supplied to keep the solids in suspension and maintain aerobic condition. A comparison of the air supplied to the laboratory activated-sludge pilot plant with that supplied to actual sewage treatment plants (Table 18) shows that the former amount appeared sixteen times too high. However, the air supplied in the lab pilot plant was often limited by the mixing condition of the liquid. In an actual sewage treatment plant, a minimum airflow of approximately 280 l/min per meter length of the aeration tank is required for adequate mixing and to avoid deposition of solids. The airflow rate in the laboratory plant was only 93 l/min per meter length of the aeration tank. The width of the laboratory unit, however, is many times smaller than that of an actual activated-sludge plant.

Evaluation of Leachate Additions to the Activated Sludge Unit

Immediately after introduction of the leachate at 0.5% of the sewage flow into the test unit on August 31, 1973, the effluent characteristics showed some deterioration as compared to the control unit (Figure 73). The average COD and BOD of the test unit were 28 mg/l and 4.3 mg/l, respectively while they were 16 mg/l and 3.1 mg/l for the control unit, respectively. However, toward the end of the 0.5% leachate addition both the effluent BOD and COD values tended to converge, while the BOD in the effluent of the test unit decreased to 2 mg/l.

Table 18

The Amount of Air Supplied to the Laboratory Activated Sludge Units as Compared with that Supplied to Actual Sewage Treatment Plants

	Air Flow Rate		Dissolved Oxygen Concentration, (mg/1)		Ratio of Air to BOD_5*	Required in the Sewage Treatment Plant**
Compartment	1/min	1/1·min	Test Unit	Control Unit	m^3/kg BOD_5	m^3/kg DOD_5
First	11.8	0.59	1.0	1.2	average 201.5	12.8
Second	9.4	0.47	3.0	4.0		
Third	9.4	0.47	5.0	6.0		

*Leachate/sewage = 2.0%; F/M = 0.3 mg BOD/mg MLVSS·day

**The Ten States Standard

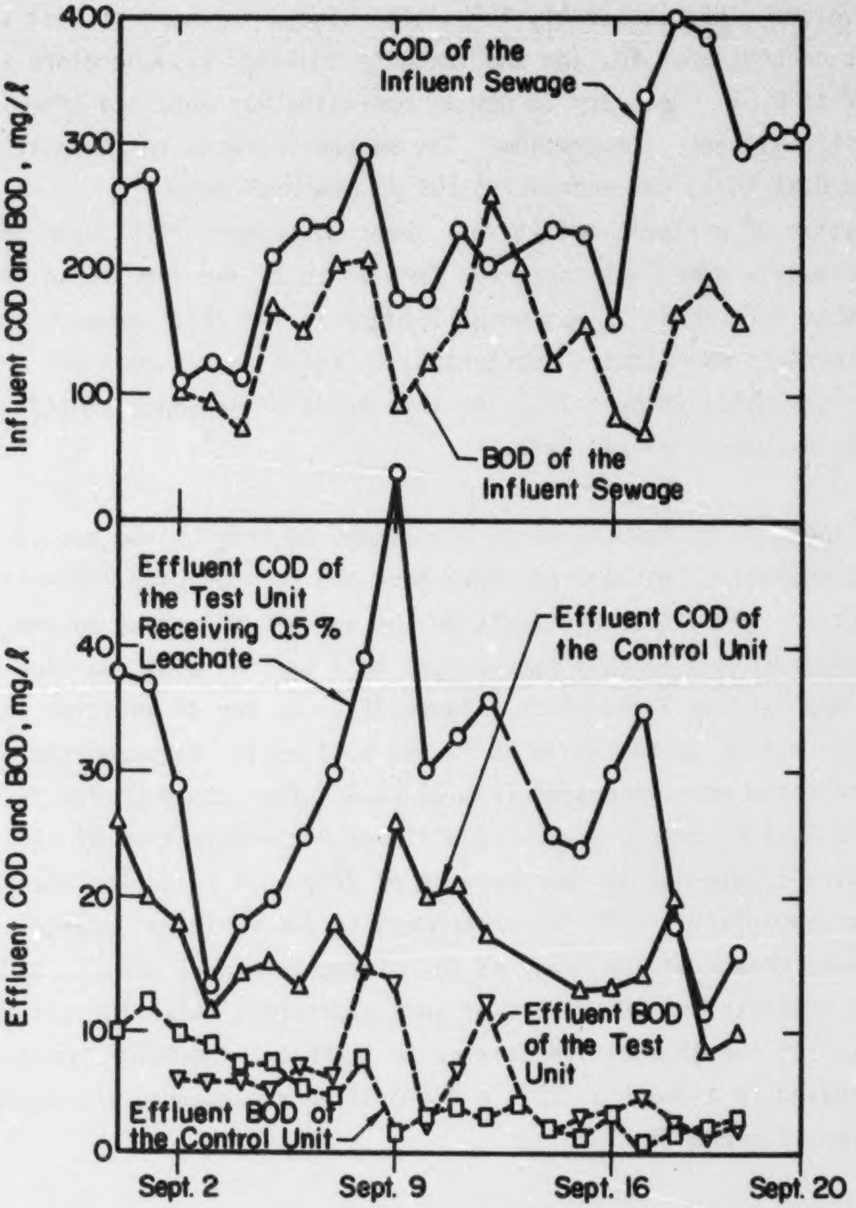

Figure 73. Influent and effluent COD and BOD concentrations of the test and control unit receiving 0.5 percent by volume of leachate

After approximately one week of steady operation at a leachate addition of 0.5% the amount added to the test unit was increased to 1% leachate by volume on September 21, 1973. The sludge in the test unit started to bulk on September 28, and the leachate addition was therefore reduced back to 0.5%. Recovery to normal operation was obtained after one additional week of operation. The second increase in leachate addition from 0.5% to 1% was successful and no abnormal deterioration of effluent quality was observed (Figure 74). When the amount of leachate added was increased from 1% to 2% and from 2% to 3% no further deterioration was noted (Figure 75 and 76). However when 4% of leachate was added a substantial increase in effluent BOD concentration was noted (Figure 77). At this level of leachate addition the sludge started to bulk excessively.

The impaired effluent quality and sludge bulking of the activated-sludge unit receiving leachate may have been due to phoshpate limitations. As a result of the leachate addition the soluble phosphate concentration decreased significantly from 4 mg/l to 1 mg/l at 0.5% addition and to 0.4 mg/l at the 1% addition (Figure 78). At the 4% addition the effluent concentration decreased to as low as 0.03 mg/l. Although the influent BOD/P ratio only increased from 22 to 50 after the 0.5% leachate addition, the relative large decrease of effluent P concentration at this addition is most likely due to the presence of 2200 mg/l Fe in the leachate to form precipitates with the phosphorus in the municipal sewage. The gradual change of the color of the sludge from dark gray to brown would also indicate the occurrence of such a process. When the effluent BOD values at the 4% addition started to increase, the BOD/P ratio had increased to as much as 200; a ratio often recommended for sustained bacterial growth is 100.

A summary of the effluent BOD and COD concentrations at the different leachate additions is presented in Figure 79. A comparison of the test and the control unit shows that increasing leachate additions do not greatly affect effluent BOD values except at the 4% addition. The COD

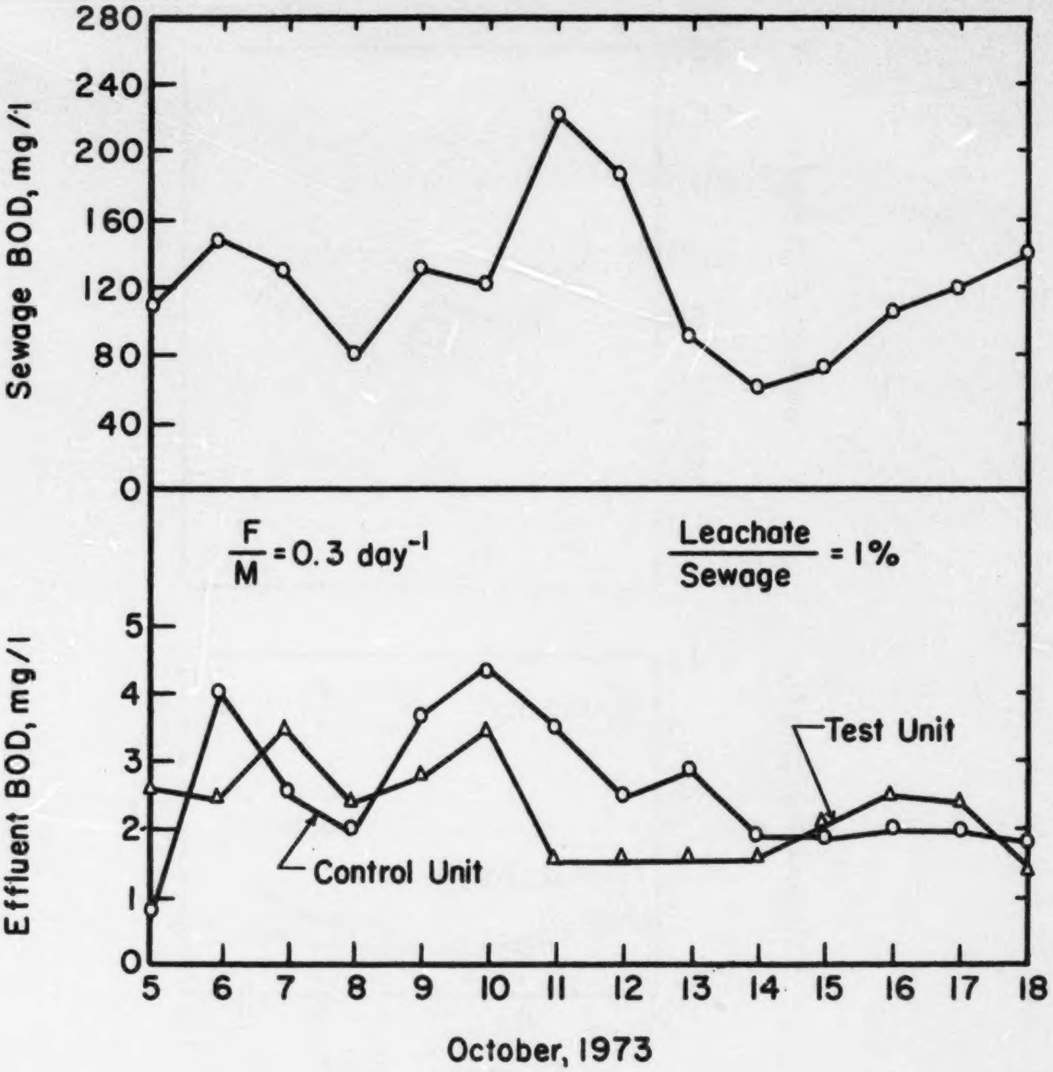

Figure 74. The Effect of 1% Leachate Addition on Effluent Quality of the Activated-Sludge Process

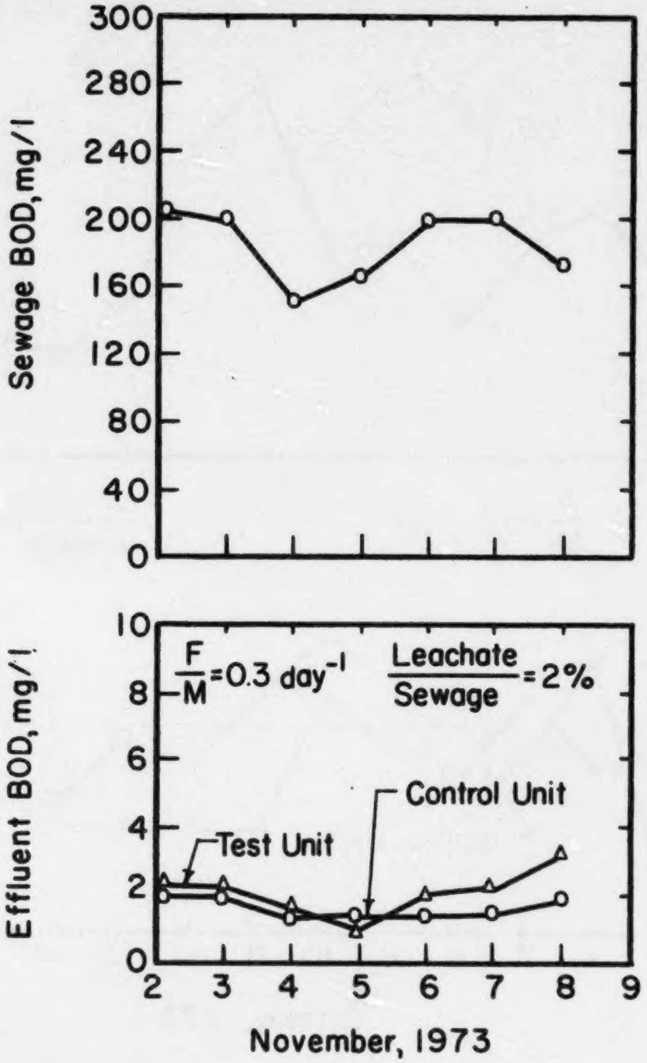

Figure 75. The Effect of 2% Leachate Addition on Effluent Quality of the Activated-Sludge Process

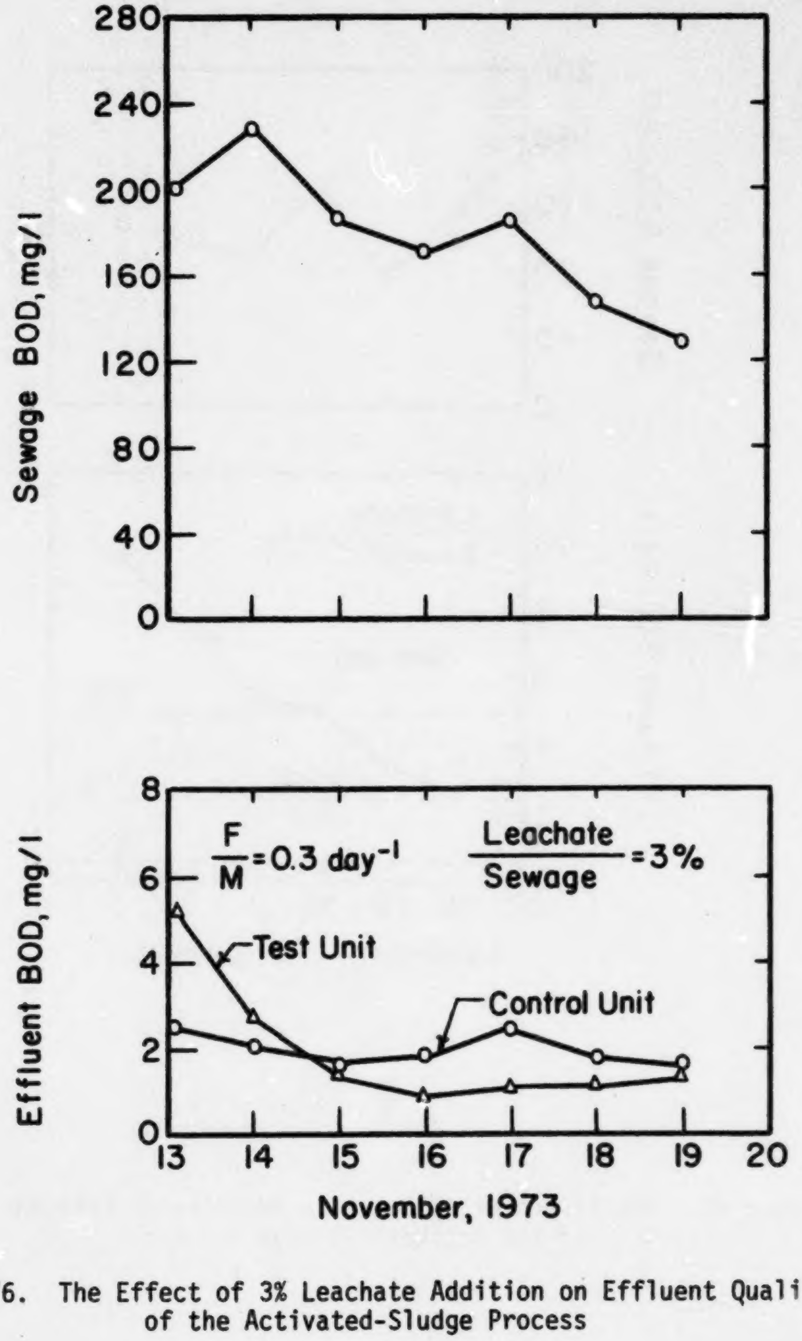

Figure 76. The Effect of 3% Leachate Addition on Effluent Quality of the Activated-Sludge Process

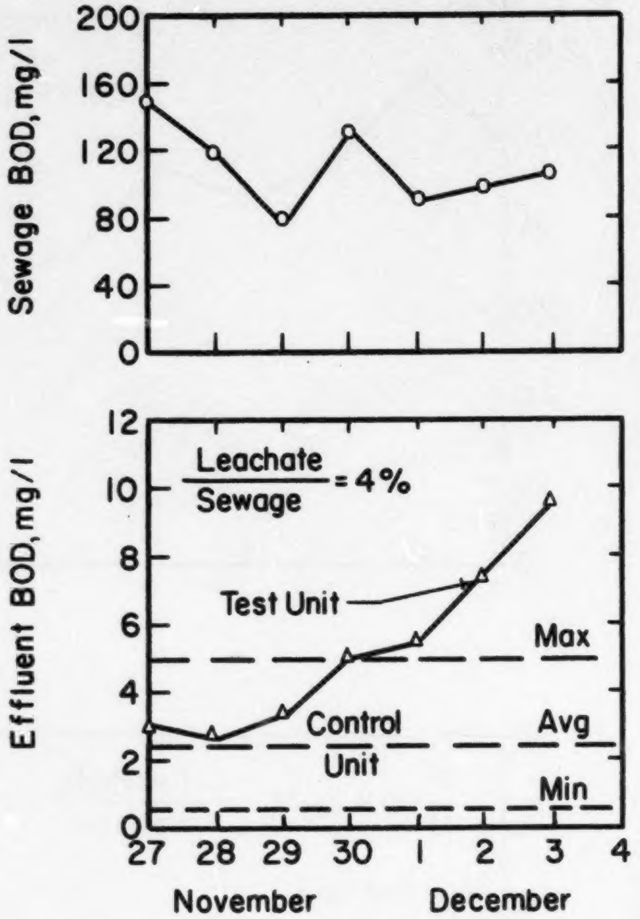

Figure 77. The Effect of 4% Leachate Addition on Effluent Quality of the Activated-Sludge Process

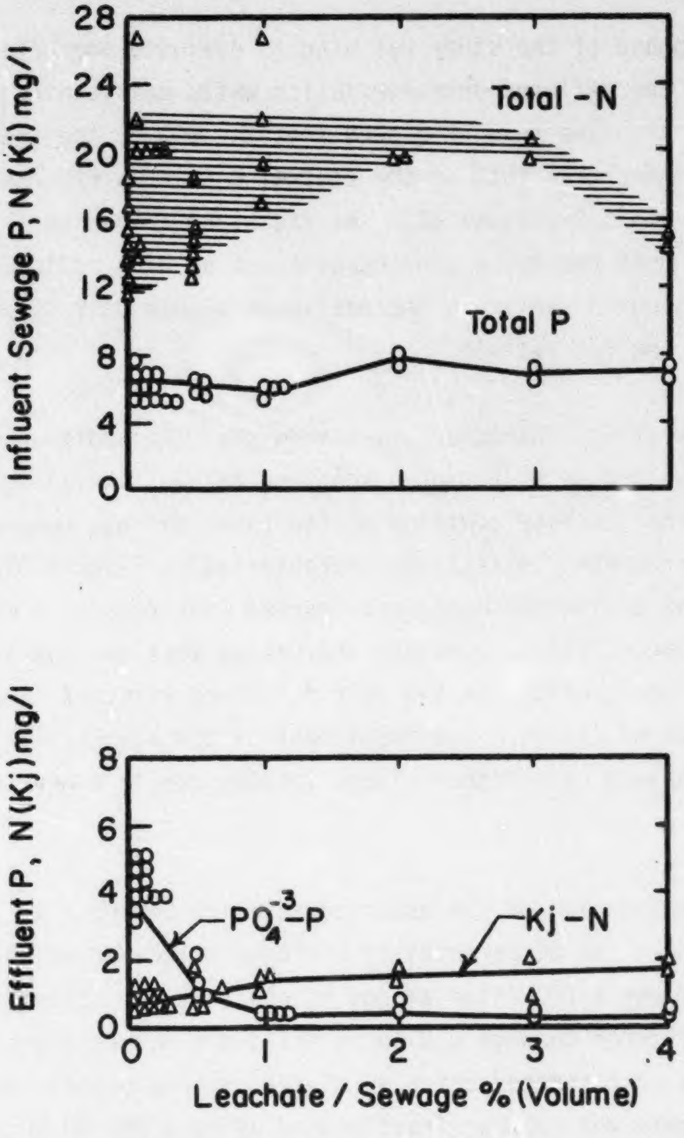

Figure 78. The Effect of Leachate Additions on the Concentration of PO_4^{-3}-P and $N(K_j)$ in the Effluent of the Best Unit

however, shows a gradual increase from 30 mg/l to 71 mg/l at the highest leachate addition. The yellow color of the effluent of the test unit showed an increase parallel to the COD values.

The second phase of the study was used to evaluate the effect of increasing loadings on the effluent characteristics while maintaining a leachate addition of 2%. The results showed that the BOD of the test unit was consistantly higher than that of the control unit at a F/M ratio of 0.6 (Figure 80) and 1.0 (Figure 81). At the highest loading the effluent BOD of the test unit reached a concentration of as high as 10 mg/l, indicating that with leachate additions the activated sludge unit is preferrably operated at low F/M ratio's.

The sludge settling characteristics show that the addition of 0.5% leachate resulted in a decreased settling rate of the sludge interface; increasing the leachate addition at the same loading, however, did not further deteriorate the settling characteristics (Figure 82). A conclusion parallel to the above one was reached with regard to the effluent phosphate concentration, possibly indicating that the low soluble phosphate concentrations in the unit interfere with the floc formation of the activated sludge. The impairment of the sludge settling was even more noticeable at the higher sludge loading due to a greater phosphorus limitation.

A further explanation of the observed settling behavior in the test unit can be found in the differences in effluent molecular weight distribution. For that purpose a 200 liter amount of effluent was collected from both units and filtered through a 0.45 m Millipore membrane whereafter the filtrate was concentrated using an AS-197 reverse osmosis membrane. The RO retenate was further fractionated using a 500 MW UF membrane as described by DeWalle and Chian (1974). While 43% of the soluble TOC of the control unit was retained with the 500 MW UF membrane, only 35% was retained in the effluent of the test unit. When the 500 MW UF retentate was applied on a Sephadex G-75 column the TOC distribution showed that the excluded fraction, eluted first, and having a molecular

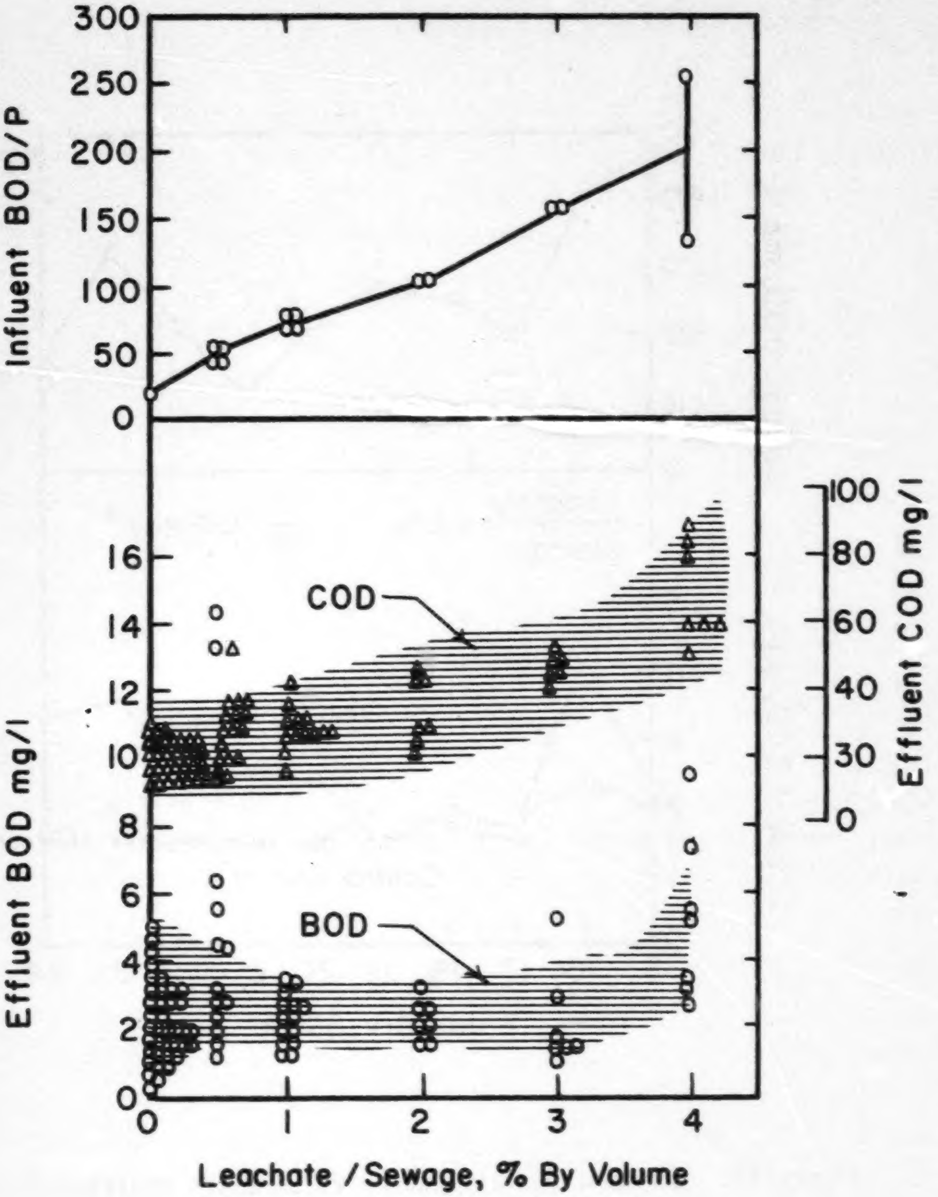

Figure 79. The Effect of Increased Leachate Additions on the Influent BOD/P Ratio and the Effluent COD and BOD Concentrations of the Test Unit

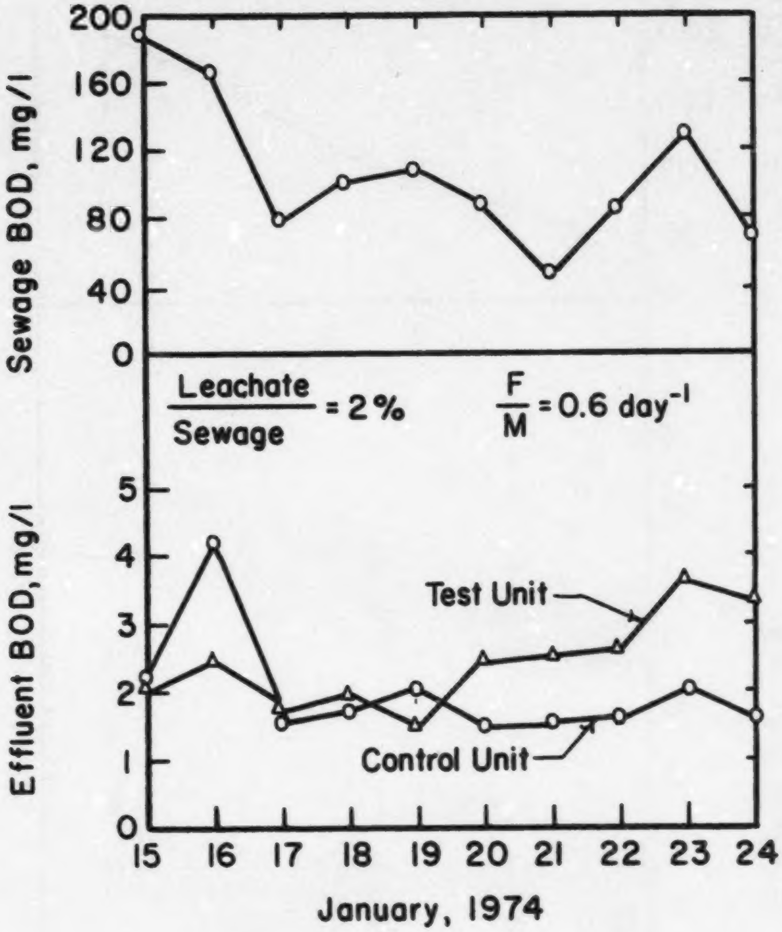

Figure 80. Effluent Quality During 2% Leachate Addition at the 0.6 F/M Ratio

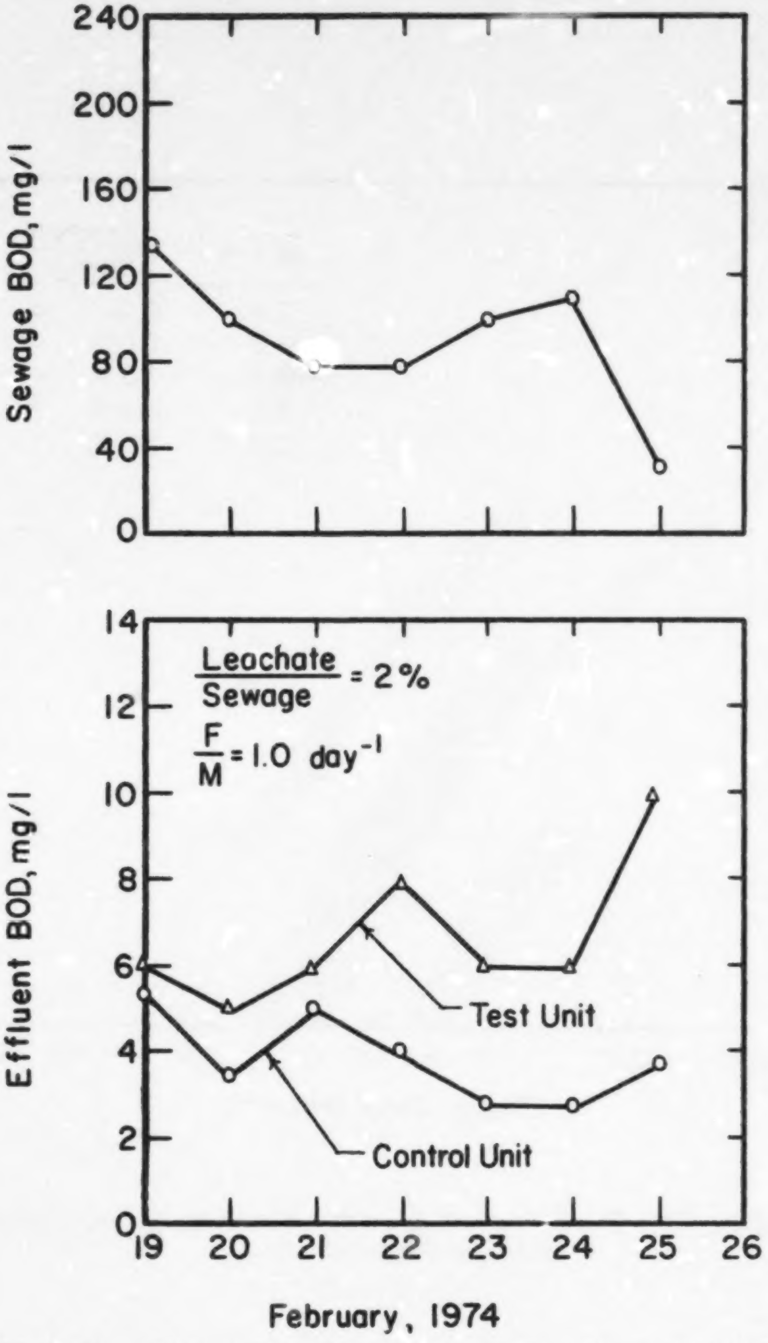

Figure 81. Effluent Quality During 2% Leachate Addition at the 1.0 F/M Ratio

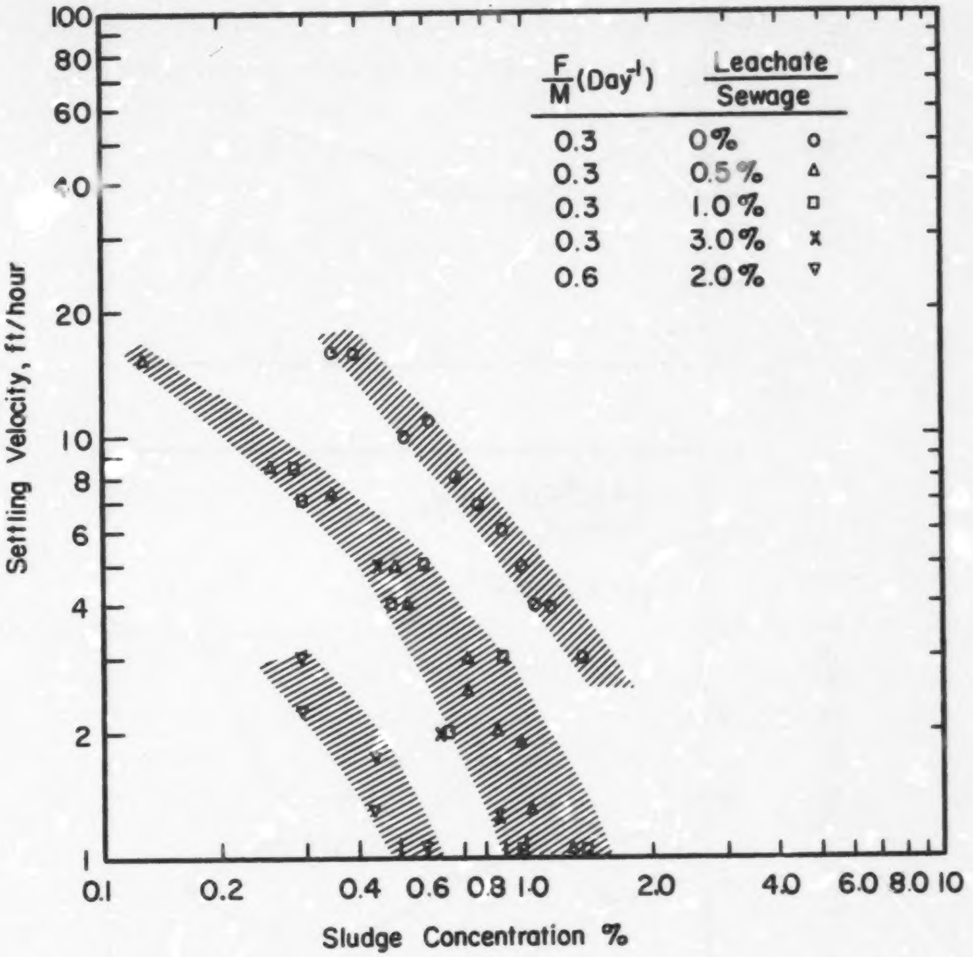

Figure 82. The Effect of Leachate Addition on the Sludge Settling Characteristics

weight greater than 30,000, was of equal size in both the effluent of the test and control unit. The low molecular weight fraction eluted last from the Sephadex, however, was smaller in the effluent of the test unit. Considerable differences were further noted for the relative composition of the different molecular weight fraction. The result of the aromatic hydroxyl-carbonyl- and carboxyl group analysis are generally comparable. However, noticeable differences were observed for the results of the carbohydrate analysis (Figures 83 and 84). While approximately 28% of the high molecular weight fraction in the control unit consisted of carbohydrates, only 21% of the organics in the high molecular weight fraction of the test unit consisted of carbohydrates. While the low molecular weight fraction of the organics in the control unit did not contain much carbohydrates, much larger concentrations were noted in the similar fraction of the test unit. Since the carbohydrates in the high molecular weight fraction tend to affect the sludge flocculation, the lower content in the high molecular weight organics of the test unit may be responsible for the decreased sludge settling rates resulting from smaller sludge flocs (DeWalle and Chian, 1974b). The low molecular weight fraction retained with the 500 MW UF membrane and included in the Sephadex G-75 generally shows the highest adsorptive capacities as compared to other molecular weight fractions. The higher carbohydrate content in the low molecular weight fraction of the test unit could therefore result in a lower adsorptive capacity in an activated carbon column.

The last phase of the activated sludge study therefore evaluated the adsorptive behavior of the soluble organic matter in the effluent of both units. The effluent was therefore filtered through a 0.45 μm Millipore membrane and passed through a 30 cm long carbon column at a superficial flow velocity of 10 cm/min (2.5 gpm/ft^2) to give an empty bed detention time of 3 minutes. The results in Figure 85 clearly show that at the low F/M loading the organics in the control unit adsorb better than those of the test unit, which may be due to the differences

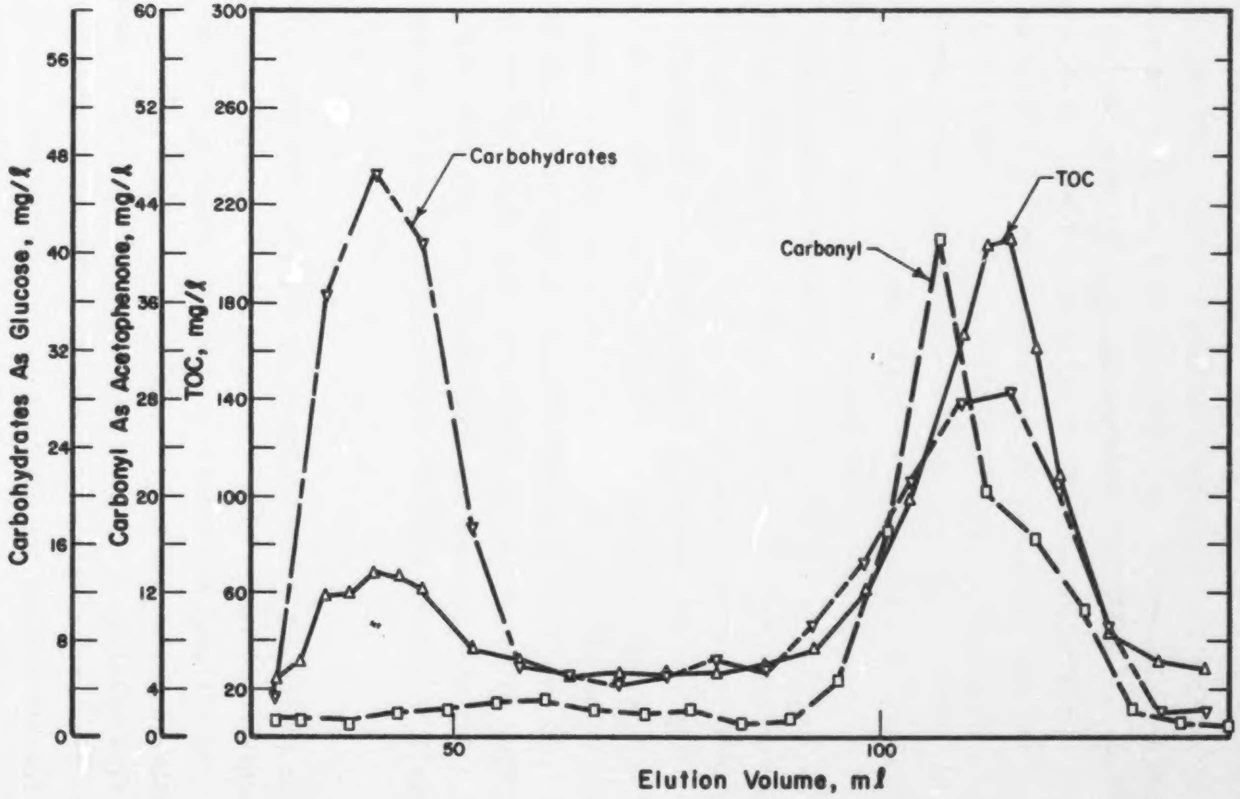

Figure 83. Elution Profile of the 500 MW UF Retentate of the Control Unit on a G-75 Sephadex Column as Characterized by TOC, Carbohydrates and Carbonyl Groups

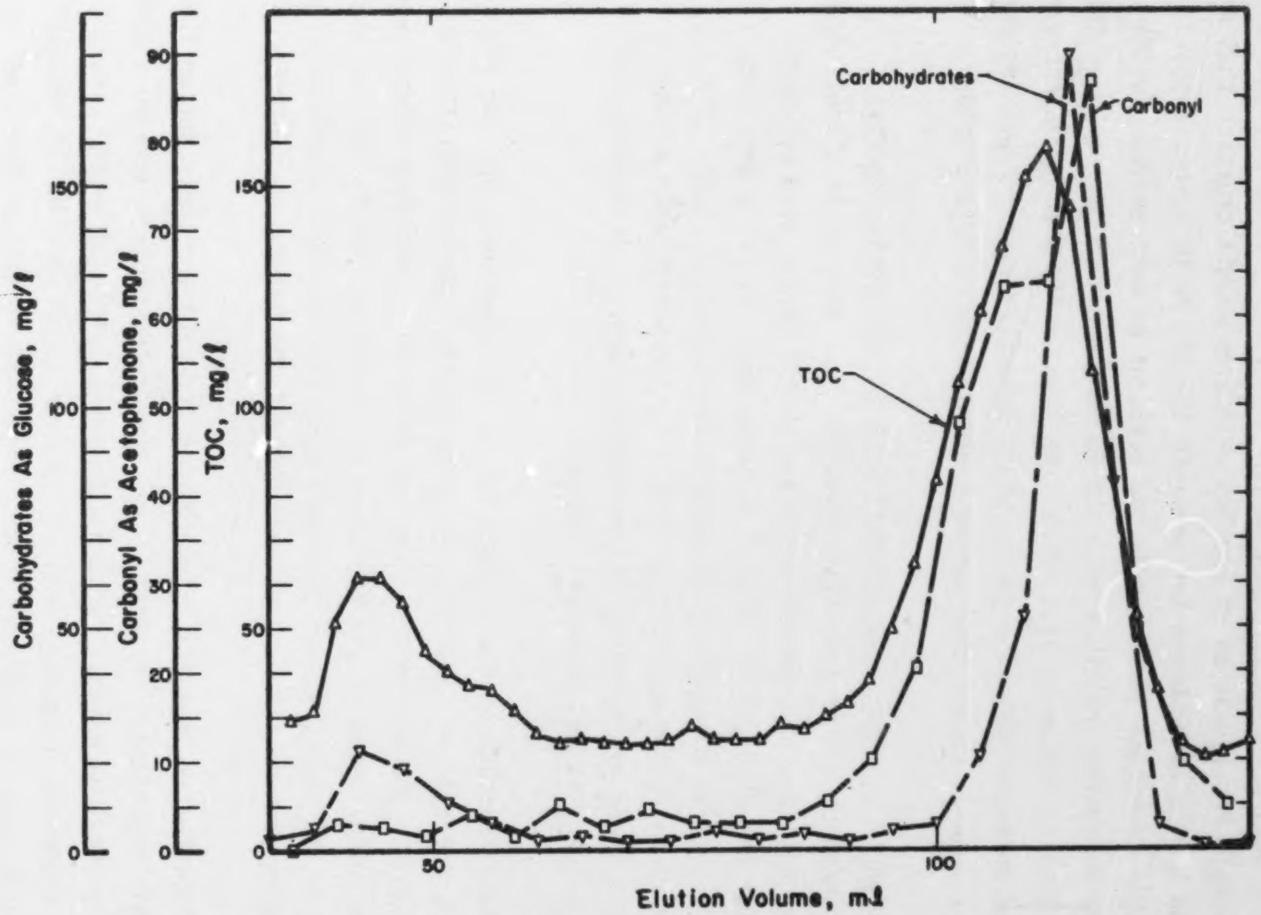

Figure 84. Elution Profile of the 500 MW UF Retentate of the Test Unit Receiving 0.5% Leachate on a G-75 Sephadex Column as Characterized by TOC, Carbohydrates and Carbonyl Groups

in both the molecular weight distribution and the composition of each molecular weight fraction. When the F/M ratio was increased to 50% for both units. Fractionation of the low molecular weight organics that are retained by the RO membrane but permeate the 500 MW UF membrane showed that their magnitude increased in the effluent of both units. Furthermore the percentage retained with the RO membrane also decreased at the higher loading (Chian et al., 1977). At high loadings bacteria excrete more low molecular weight organics which generally have a lower adsorptive capacity towards carbon than larger organics such as fulvic acids.

Evaluation of Leachate Sludge Addition to the Anaerobic Digester

The performance of the anaerobic digesters receiving waste sludges from both the test and the control-activated sludge units, were monitored daily for gas production. Figure 86 shows that the daily gas production rates of the two anaerobic digesters is approximately equal. There appears therefore no deleterious effect on the performance of the anaerobic digester receiving sludge from the test unit treating the combined leachate and municipal sewage.

The characteristics of the sludges fed to the digesters, and the digested sludge are listed in Table 19. In spite of the high concentration of iron found in the sludge from the test unit, no undesirable effects were observed with regard to the operation of the unit. The release of the iron from the solids to the supernatant by the anaerobic digestion process was negligible and represented only 0.3% of the total iron content.

It is important to establish the fate of iron and phosphate during the anaerobic digestion of sludges. The iron in the waste-activated sludge may be present as either ferric hydroxide or ferric phosphate precipitates. In the anaerobic digester, most of the iron is present in the reduced Fe^{2+} form. The iron concentrations in the supernatant of the test and control digesters were 4.0 mg/l and 1.6 mg/l respectively; these values are higher than predicted from the $FeCO_3$ solubility, which in turn depends on the partial pressure of CO_2 in the gas phase. Furthermore, because

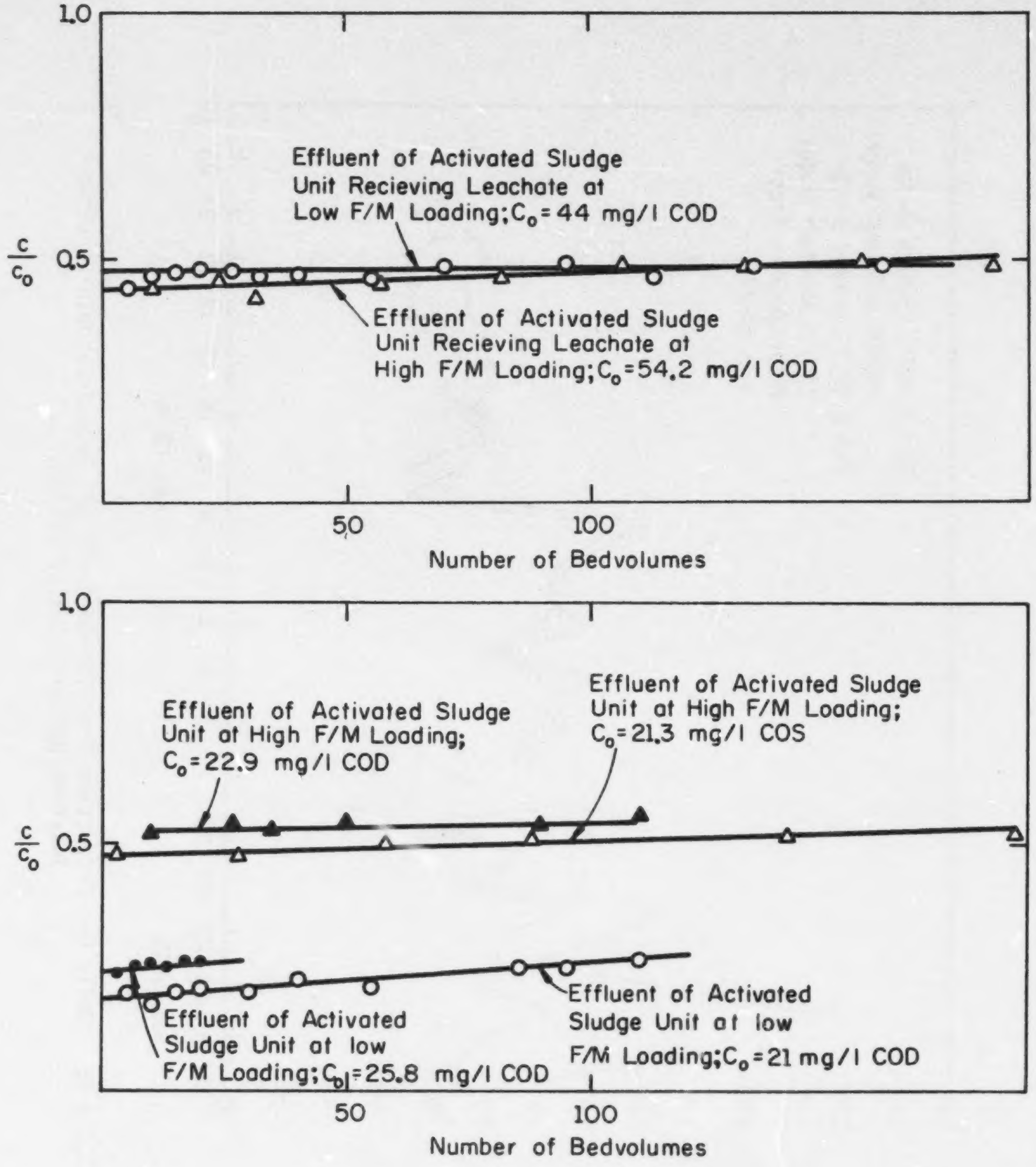

Figure 85. Adsorptive Character of the Soluble Organic Matter in the Effluent of the Test and the Control Unit Both Operated at F/M ratios of 0.3 and 0.6

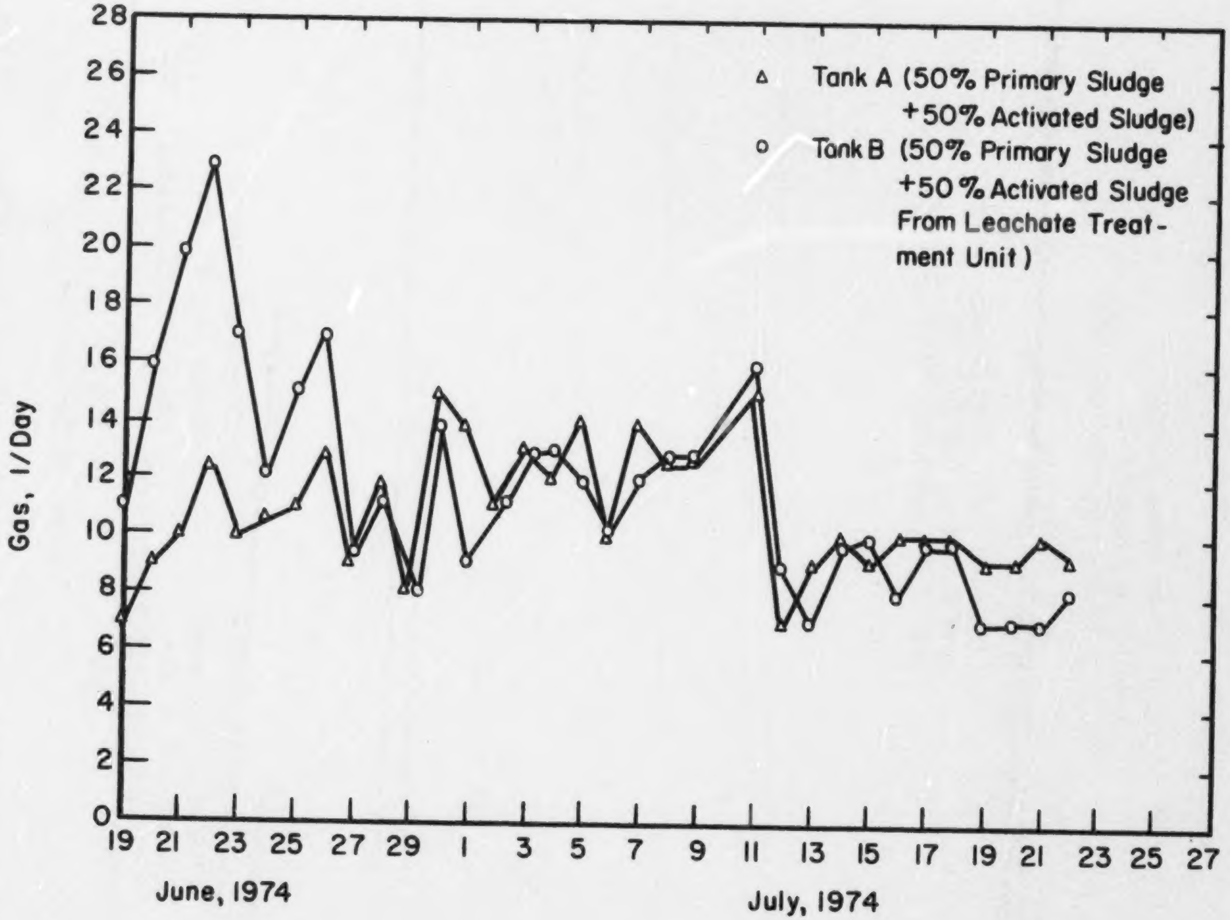

Figure 86. Daily Gas Production from the Control- and Test Anaerobic Digestor Treating Waste-Activated Sludge

Table 19

Anaerobic Digestion of the Waste-Activated Sludge from the Leachate Treatment

	Feed Sludge		Digested Sludge	
	Control Unit	Test Unit	Control Unit	Test Unit
pH	7.0	7.0	6.9	7.0
Total Solid (%)	2.54	3.10	1.72	2.19
Volatile Solid (%)	1.85	2.10	1.00	1.21
Ratio VS/TS	0.728	0.677		
VS Reduction (5)	46	42		
Total Fe mg/l	480	1.360	1.6*	4.0*
Total P mg/l	290	282	14.13*	12.25*
Gas production, l/kg	288	278		
VS Reduction				

*Concentrations in the supernatant

different levels of soluble iron were present in these two units, it is believed that the solubility of the ferrous carbonate is not the limiting factor for the solubilization of iron in the digester.

The ferrous iron may also react with sulfide or phosphate to form the relatively insoluble ferrous sulfide ($K_{so} = 4 \times 10^{-19}$), or vivianite (ferrous phosphate, $K_{so} = 10^{-30}$). However, the amount of sulfide ion in the anaerobic digester was relatively low due to the low sulfate concentration in the sewage, as the average concentration of sulfate is approximately 100 mg/l as SO_4^{-2} or 33 mg/l as S^{-2}, and the total phosphorous concentration in the digester is 300 mg/l only, not enough is available to precipitate all of the 1,360 mg/l iron present in the test unit.

The only remaining mechanism that could explain the retention of iron in the suspended solids of the digested sludge is an adsorption process in which the iron hydroxides adsorb onto the sludge particles. This possibility is supported by the result of the analysis shown in Table 19, as a higher concentration of ferrous ion in the supernatant, corresponds to a larger amount of iron adsorbed onto the sludge. This agrees with general equilibrium conditions established between the adsorbate iron and adsorbent sludge. The lower soluble total-P observed in the supernatant of the digested sludge from the test unit corresponds with the higher concentration of iron on the supernatant. This correlation was also noted by Singer (1972).

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VI

ESTIMATED COSTS FOR LEACHATE TREATMENT

CONCLUSIONS

It was found that aerated lagoons provide the least expensive method of treating leachates having comparatively low BOD_5 values (e.g., 5,000 mg/l) and relatively high flow rates (e.g., 20 gal/min). As the BOD_5 level of the leachate increases at the same high flow rate, the treatment cost using anaerobic filters becomes increasingly attractive, and at a BOD_5 value of 25,000 mg/l it equals that of the aerated lagoon process if credit for the methane gas produced is deducted. Taking into consideration the treatment level and thus the effluent quality, the combined treatment of leachate and domestic wastewater using the activated sludge process becomes most desirable because of the high dilution factor, especially when the leachate BOD_5 levels are low and the flow rates are high.

In minimizing the impact of the treated leachate on the environment, the treatment of leachate using aerated lagoons and physical-chemical treatment processes (such as a combination of slow sand filtration, activated carbon adsorption, and reverse osmosis) is most effective, although such treatment would cost somewhat more than combined treatment of leachate and domestic wastewater with activated sludge at high leachate flow rates and low BOD_5 levels. The difference in treatment costs between the two approaches narrows, however, as the leachate flow rates decrease and the BOD_5 levels increase.

INTRODUCTION

The cost estimates presented in this section are intended to aid solid waste management planners, decision makers, and design engineers in selecting alternative on- and off-site leachate treatment methods to achieve a designated level of treatment for leachates of various strengths and flow rates.

The leachate flow rates and BOD_5 levels examined in this study were 2 and 20 gal/min,* and 5,000 and 25,000 mg/l, respectively. These values were selected so that a broad range of leachates produced by various landfill sites could be considered. In view of the high BOD_5 levels and the objective of low treatment cost, biological processes were selected for first-stage treatment. The costs of physical-chemical treatment processes were estimated only for cases where such processes would be used to treat the effluents from aerated lagoons and anaerobic filters.

The cost comparison is based upon the results of this study on leachate treatment, on the assumption set forth in this chapter, and on the average estimating data from two recent EPA reports (Black and Veatch, 1971; Bechtel, 1975). All costs were then updated to August 1977 according to the Water Quality Office Wastewater Treatment Plant Index (Engineering News Record, January 1971, January 1975, August 1977).

The user must recognize certain limitations in using the cost estimates presented. Estimates based upon treatment data obtained from the laboratory studies and upon average cost estimating data should be considered only of sufficient accuracy for use in reaching broad, general conclusions. When used with sound judgment by knowledgeable persons, the data can be useful in selecting appropriate treatment processes for a specific leachate based upon known levels of contamination and flow rates.

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*1 gallon = 3.79 litre

It should also be realized that the cost estimates presented in this section must be revised and updated periodically since waste treatment costs are continually changing and since new and improved waste treatment techniques and methodologies are rapidly emerging.

METHODS AND PROCEDURES

Activated Sludge

The cost estimates for the combined treatment of leachate and municipal wastewater were based on the addition of leachate at a level of 1 percent by volume to the sewage when the nominal daily flow rate of the leachate is 30,000 gallons (20 gpm). The proportion of leachate added was reduced to 0.1 percent by volume when its flow rate decreased to 3,000 gallons per day (2 gpm). If the leachate represents 1 percent of the flow into the municipal treatment plant, the overall flow rate of the plant must be 3 MGD.

The BOD_5 level of the municipal sewage introduced into the activated sludge system from the primary sedimentation basin is typically 140 mg/l. When 1 percent of leachate having a BOD_5 of 25,000 mg/l is added, the BOD_5 of the combined wastewater becomes 390 mg/l (140 + 1% of 25,000), corresponding to a 279 percent increase in sewage strength. To maintain the same effluent quality, the municipal treatment plant should therefor have the capacity to treat the equivalent of 8.4 MGD of sewage having a BOD_5 of 140 mg/l. Also, a 280 percent decrease in sludge settling rate was also observed in this laboratory when leachate was added at 1 percent. Again, to counteract this effect the municipal treatment plant facilities should be expanded to the equivalent of 8.4 MGD to maintain the same effluent quality. The increase in treatment cost resulting from the need for larger aeration and sedimentation basins, a greater air supply, larger anaerobic digesters, and increased sludge disposal is attributable to treating the specific leachate under study. The additional costs of transporting the leachate through pipelines and by trucking were also considered.

The calculations of the aeration basin volume requirements were based upon an F/M ratio of 0.3 day^{-1} and a MLVSS of 2,000 mg/l. A yield of 0.65 g VSS/g BOD_5 was used for sewage and 0.80 g VSS/g BOD_5 for leachate. A factor of 0.8 was used to convert MLSS to VSS.

Cost figures based upon the total costs of treating 1000 gallons of sewage influent having a BOD_5 of 140 mg/l and at a specific plant capacity as given by Bechtel (1975) were used to arrive at the costs for conventional activated sludge treatment, anaerobic digesters, and sludge drying. A factor of 1.25 was then used to update the costs to August 1977 based on the average cost indexes given by Engineering News Record (McGraw Hill) between January 1975 and August 1977. The costs of transporting leachate by pipeline were calculated assuming the use of 3-in.-diameter, schedule-40 PVC pipe for a distance of 15 miles at an available pumping head of 75 psig. Data given in Costs of Process Equipment (Chemical Engineering, March 1964) were used to estimate the costs of installed cross-country pipeline. A factor of 2.71 was used to update these costs to August 1977. For smaller quantities of leachate, a trucking cost of 7.5¢/100 lb of liquid for a distance of 30 miles round trip was used.

Aerated Lagoon

The design criteria for an aerated lagoon to treat leachate were as follows:

BOD_5 removal	99%
Mean Cell Residence	90 days (BOD = 25,000 mg/l)
Time	30 days (BOD = 5,000 mg/l)
MLVSS	8000 mg/l (BOD = 25,000 mg/l)
	6000 mg/l (BOD = 5,000 mg/l
Y	0.8 g VSS/g BOD
kd	0.025 day^{-1}
Aerator	2 lb O_2/hp-hr under field conditions
BOD_5:P	150:1
BOD_5:N	20:1
Sludge Production	g VSS/0.8
Sedimentation Basin	400 gpd/ft^2

Design equations given in Wastewater Engineering (Metcalf & Eddy, 1972) were used to determine variables such as the volume of the aeration basins and the oxygen requirements.

The capital (including engineering costs), operation, and maintenance costs were estimated from the Black and Beatch report (1971). The installed costs of the basins were increased 15% to cover the piping costs. A factor of 1.78 was used to update the costs to August 1977 based on the average cost indexes given in Engineering News Record (McGraw Hill) between January 1971 and August 1977. The costs of ammonia and phosphoric acid were taken from the August 1977 issue of Chemical Marketing Reporter (Schnell Publishing Co.) Costs of \$120/ton for ammonia and \$3.20/100 lb for agricultural-grade phosphoric acid (52-54% available phosphoric acid) were used. The land cost was estimated at \$5,000/acre. For electrical energy, a cost of 3 cents/KWH was used. An average pay rate of \$10.00 per man-hour, including overhead costs, was used in estimating operating and maintenance costs. Capital equipment was depreciated on a straight-line basis over a period of 10 years for moving equipment and 20 years for fixed installations. Interest charges were computed at the rate of 4 percent of the initial capital investment over the entire period.

Anaerobic Filter

The design criteria used for estimating the costs of treating leachate with an anaerobic filter were as follows:

BOD_5 Removal	97%
Loading	0.31 Kg BOD_5/M^3 day
Yield, VSS	0.024 g VSS/g BOD_5
Detention time	87 days (leachate BOD = 25,000 mg/l)
	16 days (leachate BOD = 5,000 mg/l)
Recirculation Ratio	20:1
Yield, Methane	1.75 liters (78% CH_4)/g TOC

The capital investment estimate was based on the use of a rubber-lined steel tank and B.F. Goodrich vinyl core packings along with the necessary arcillary equipment such as pumps and piping. The costs of the rubber-lined vessel and pumps were obtained from equipment cost data (Chemical Engineering, ENR = 400 for materials; Chemical Engineering, March 16, 1977). Factors of 2.75 and 2.71, respectively, were used to update the costs to August 1977. A verbal quote was obtained from B.F. Goodrich Co. for the vinyl core packings ($2.75/cu ft installed) on August 19, 1977. The operating costs were computed in the same way as for the aerated lagoon; the maintenance costs used, however, were 5 percent of the capital investment on an annual basis.

Slow Sand Filtration

The cost estimates for the slow sand filtration unit were based upon a single data point: a unit of comparable capacity installed recently by Daily and Associates Engineers, Inc. (Champaign, IL 61820). A rather conservative flow rate of 8 gallons/day-ft^2 was used in the design of the filter. The operating and maintenance costs were calculated using the previously described methods of computing costs such as depreciation, interest, and maintenance.

Activated Carbon

Based upon both the batch isotherm and the column data, the design criteria for the activated carbon unit were as follows:

Influent TOC*	200 mg/l from aerated lagoon (AL) 600 mg/l from anaerobic filter (AF)
TOC Removal	75%
Color Removal	90% measured at 400 nm
$(X/M)_0$	0.15 g TOC/g Carbon (AL) 0.10 g TOC/g Carbon (AF)
Activated Carbon	Filtrasorb 400
Contact Time	2 hours
Pretreatment	Slow sand filter

The capital investment was estimated by extrapolating the cost data provided by Bechtel (1975). After being updated to August 1977, this cost was $1.0/1000 gal. The operation and maintenance costs were also obtained from Bechtel (1975). The cost of activated carbon used was $0.65/lb.

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*The influent TOC will be 1/5 of that while using leachate having a BOD_5 of 5,000 mg/l instead of 25,000 mg/l.

Reverse Osmosis

The design criteria for the reverse osmosis process were as follows:

Pretreatment	Slow Sand Filtration, activated carbon column, and 5 μ prefilter
Product Water Recovery	90%
TDS Removal	95%
TOC Removal	80%
Module	DuPont Hollow Fiber
Pressure	600 psig

The cost estimates for reverse osmosis using DuPont's B-10 modules were based upon average cost data obtained from the manufacturers as of August 1977. Average costs of \$1.67/gallon/day (gpd) and \$3.33/gpd were used for the 30,000 gpd and 3,000 gpd plants, respectively. The power requirements are 20 hp for a 30,000 gpd unit and 2 hp for a 3,000 gpd unit. Unlike activated carbon treatment processes, operating costs for reverse osmosis treatment are relatively insensitive to the levels of contaminants in the feed. The depreciation costs are based on 10-year life for the mechanical parts and a 3-year life for the membrane modules. Other costs for operation and maintenance are similar to those used in the previous calculations.

RESULTS AND DISCUSSION

Using the procedures outlined in the previous section, cost estimates were obtained for treating leachates at two BOD_5 levels and flow rates. The results are presented in Table 20. To estimate the cost of treating combined leachate and activated sludge, fixed costs of $2/1000 gal and $6/1000 gal of leachate were added for transporting leachate at flow rates of 20 gpm (30,000 gpd) and 2 gpm (3,000 gpd), respectively. The $2/1000 gal value is for transporting leachate by pipeline, while the $6/1000 gal figure is for hauling it by trucks within a radius of 15 miles (i.e., 30 miles round trip). To transport leachate at a flow rate of 2 gpm by pipeline would cost around $15/1000 gal even if the pipeline is depreciated over a 20-year period. It should be realized that the use of a 20-year period to depreciate fixed installations may not be realistic, since the strength of the leachate produced would be reduced greatly over such a period.

It can be seen from Table 20 that the aerated lagoon provides the least expensive method of treating leachate having a comparatively low BOD_5 value (e.g., 5,000 mg/l) and relatively high flow rate (e.g., 20 gpm). At a 20 gpm flow rate, as the BOD5 level of the leachate increases the treatment cost using anaerobic filters becomes increasingly attractive, and at a BOD_5 value of 25,000 mg/l it equals that of the aerated lagoon process if credit for the methane gas produced (e.g., at $1.50/1000 cu ft) is deducted. Taking into consideration the treatment level and thus the effluent quality, the combined treatment of leachate using the activated sludge process becomes most desirable because of the high dilution factor, especially when the leachate BOD_5 levels are low and the flow rates are high.

It should be noted that at high leachate BOD_5 levels (i.e., 25,000 mg/l) and at both flow rates under study the costs of complete leachate treatment using aerated lagoons and physical-chemical processes (such as a combination of slow sand filtration, activated carbon adsorption, and reverse osmosis) are comparable to those for combined treatment of leachate and domestic wastewater by

TABLE 20

A SUMMARY OF COST ESTIMATES FOR LEACHATE TREATMENT

	Leachate (gal/min)*	Typical Effluent COD (mg/l)		Costs of Treatment ($/1000 gal leachate)*	
Influent BOD, mg/l		25,000	5,000	25,000	5,000
Activated Sludge (AS) (Combined treatment)	20	30	30	23.6	6.0
	2	30	30	41.4	11.9
Aerated Lagoon (AL)	20	500	100	17.9	4.1
	2	500	100	31.6	10.0
Anaerobic Filter (AF)	20	1500	300	22.1(17.9)†	6.8(5.9)
	2	1500	300	43 (38.8)	17.7(16.8)
AL-Sand Filter (SF) -Activated Carbon (AC)	20	125	25	25.7	7.3
	2	125	25	39.9	13.7
AL-SF-AC-Reverse Osmosis (RO)#	20	25	5	27.6	9.2
	2	25	5	44.6	18.4
AF-SF-AC	20	375	75	32.8(28.6)	10.6(9.7)
	2	375	75	54.2(50)	22.0(21.1)
AF-SF-AC-RO#	20	75	15	34.7(30.4)	12.5(11.5)
	2	75	15	58.9(54.3)	26.7(25.4)

*1 gal = 3.79 litre

†Numbers shown in parenthesis indicate the costs of treatment after deducting the credit for methane produced @ $1.50/1000 cu ft.

#After RO treatment the total dissolved solids (TDS) decreased to 300 mg/l and 60 mg/l for influent leachate BOD concentrations of 25,000 mg/l and 5,000 mg/l, respectively.

activated sludge. The effluent quality is, however, far better when the complete treatment scheme discussed above is used. The COD value of the effluents from the complete treatment scheme and from the combined treatment process are 5 and 30 mg/l, respectively, whereas the TDS levels are 300 and 750 mg/l, respectively. In addition, the color-bearing materials are removed completely using the complete process. Therefore, to minimize the impact of the treated leachate on the environment the complete treatment of leachate using aerated lagoons and physical-chemical treatment processes is most desirable. As leachate BOD_5 levels decrease, however, the percentage difference, in treatment costs would be somewhat greater.

Although the information presented in Table 20 can be of particular value in establishing the effect of changes in leachate flow rates and BOD_5 levels on treatment costs, the specific costs presented should be used with caution. It should be realized that the circumstances of a particular situation may alter treatment costs drastically. For example, if the leachate were allowed to discharge into a municipal wastewater treatment plant having excess capacity, the cost (in terms of the surcharges paid) could be substantially lower than the estimates presented here.

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